A Thesis for the Degree of Doctor of Philosophy

entitled

FRIEDEL CRAFTS POLYMERS

by

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SUMMARY

The need for materials of high thermal stability, in the aerospace industry, has prompted considerable research, in recent years, in the area of high temperature polymers.

In 1964, it was shown that polymers of high thermal stability, having a polybenzyl type structure, could be synthesised from substituted aromatic monomers using Friedel Crafts catalysts. Since the discovery of Friedel Crafts polymers of this nature, considerable attention has been focussed on the kinetics of their formation, their structure and heat stability. The overall objective of work of this nature was to determine the factors which affected thermal stability in order to devise methods of synthesis of materials of optimum stability. A detailed kinetic examination of the early stages of the co-polymerisation of di(chloromethyl) benzene (DCMB) and various aromatic and heterocyclic comonomers catalysed by stannic chloride has been carried out by Grassie and Meldrum. In their work, the kinetics of the early stages of polymerisation has been related to the structure of the products before subsequent correlation with the thermal properties of the polymer.

Commercially, Friedel Crafts polymers are made by co-polymerisation of dimethoxy-p-xylene (DMPX) and aromatic comonomers and it is with this system that the present work is concerned. Kinetics of the initial stages of co-polymerisation of DMPX and benzene have been carried out, the structures of low and high molecular weight products have been

elucidated and these findings have been related to results from thermal analysis which has been carried out. Comparison of these results has been made with those of Grassie and Meldrum for a corresponding system based on DCMB.

Considerable problems were experienced in kinetic analysis of the system based on DMPX. The initial formation of an insoluble polar intermediate arising from complexing of DMPX and stannic chloride brought about initial heterogeneity thus limiting kinetic analysis. It was found that methanol, the condensation product, complexes to stannic chloride in course of polymerisation, to form a 1:1 stannic chloride:methanol complex, which is an active catalyst, before the formation of an inactive 2:1 methanol:stannic chloride complex resulting in inhibition of reaction. This problem was overcome by using large concentrations of catalyst and taking inhibition into account in calculation of rate constants.

The overall conclusion from this work, from kinetic and structural examination is that polymers prepared from DMPX are similar in basic structure to those derived from DCMB but chain branches in DMPX based polymers are shorter than those in their DCMB counterparts. Crosslinking is less in the former system and solubility is thereby greater. These features result from the lower reactivity of pendant methoxyl groups as compared with chloromethyl groups as has been established by kinetic analysis.

Crosslinking of polymers based on DMPX is possible by heating or by the use of a crosslinking agent and thermal properties of these polymers are comparable with those derived from DCMB.

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PREFACE

This work was carried out, in the Department of Physical Chemistry at the University of Glasgow, during the period October, 1971 to October, 1974, under the overall supervision of Professor G. A. Sim.

I gratefully acknowledge the financial support of the United States Air Force throughout the course of this work. I convey my thanks to my friends and colleagues of the macromolecular group for their assistance in the form of advice and useful discussion. I am indebted to the technical staff of the Department in particular to Mr. J. Gorman for assistance in thermal analysis and to the glassblowers for their technical expertise and to Miss S. M. Hector for typing.

I express my sincere gratitude to Professor N. Grassie, first of all for suggesting the project and for his patience, direction and encouragement throughout the course of this work.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Over the past fifteen years, in polymer chemistry, considerable attention has been focussed on the synthesis of polymeric materials which exhibit improved thermal properties. This work has been prompted by the need for materials of high thermal stability, particularly in the aerospace industry, where they are required for use as adhesives, protective coatings, ablative heat shields and for electrical insulation. Commercially, polymers which have satisfactory properties within the range 200°-300°C, have been prepared by Friedel Crafts type polymerisations.

Polymers produced by Friedel Crafts catalysts were first reported in 1885[1] when it was shown that they were formed by the action of aluminium trichloride on benzyl chloride and since then, considerable work has been directed towards the elucidation of the mechanism of this type of polymerisation.

In recent years polybenzyl has been the subject of numerous investigations[2-9], and promising results were obtained between 1959 and 1965[10-13], when substituted aromatics were polycondensed by Lewis acids to give polybenzyl structures which exhibit thermal and mechanical properties superior to epoxy and phenolic resins. The materials formed from these polycondensations are now known as Friedel Crafts polymers.

Friedel Crafts polymers are now available[14] commercially and extensive investigation has been carried out on the kinetics of their formation, their structure and the heat stability of the final polymer[15-25].

1.2 Mechanism of Friedel Crafts Polymerisation

Polymerisations promoted by Friedel Crafts catalysts fall into two main classes. Polymerisation of olefins, dienes and related monomers may be induced by Lewis acid catalysts, and were initially thought to proceed by a chain reaction similar to free radical polymerisations but in which the active species was believed to be cationic in nature. A well cited example of this type of polymerisation is that of styrene catalysed by stannic chloride.

A quantitative study of this reaction in dichlorethane solution[26-28] resulted in the following mechanism being proposed

$$M_1 + C \rightleftharpoons M_1^{(+)}C^{(-)} \qquad \text{initiation}$$

$$M_1^{(+)}C^{(-)} + n\,M \longrightarrow M^{(+)}n +_1 C \qquad \text{propogation}$$

$$Mn^{(+)}C^{(-)} \longrightarrow Mn + C \qquad \text{termination}$$

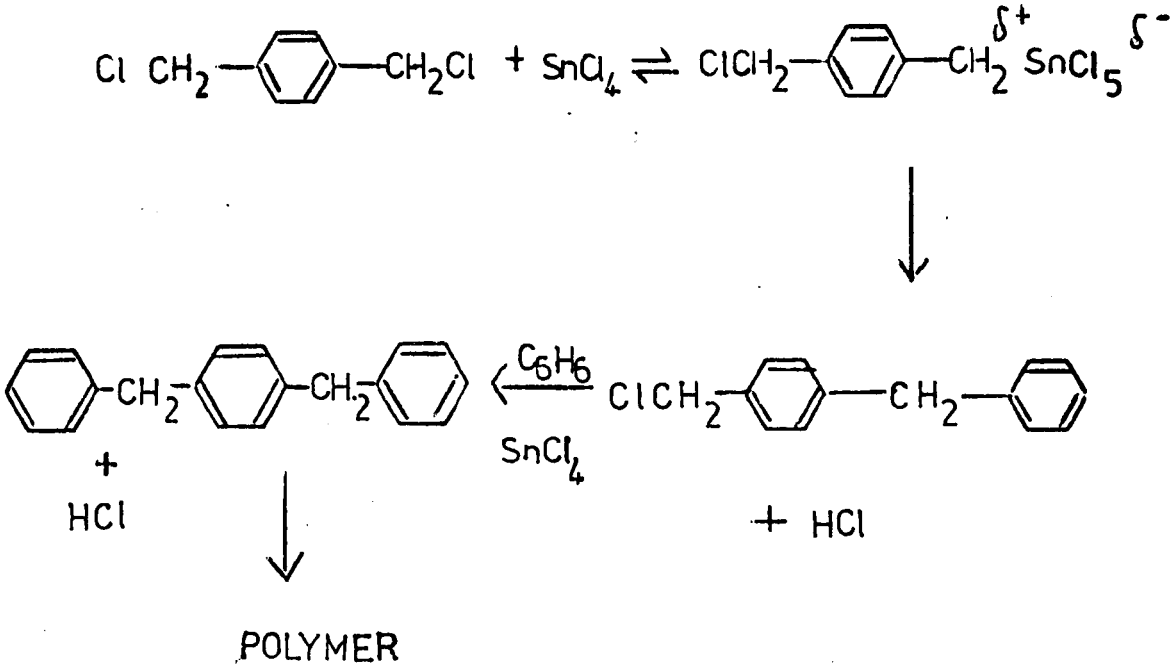
where C is catalyst

A mechanism of this nature was generally accepted until 1964 for polymerisations promoted by Lewis Acids, but there was little direct evidence for the presence of carbonium ions during polymerisation. However, the theory became firmly established as it satisfactorily accounted for most experimental observations, including the effect of increased solvent dielectric promoting rate[29] and the effect of various proton containing co-catalysts[29]. In 1964 Gandini and Plesch[30-33] compared spectral and conductivity measurements with rate in the polymerisation of styrene induced by perchloric acid. Their results suggested that the propagating species was not ionic but a highly polar ester formed from the olefin and perchloric acid which is stabilised by four styrene molecules. In many ways these highly polar species would behave similar to ions, and for this reason these polymerisations were termed pseudo-cationic polymerisations.

The discovery of this mechanism necessitates a re-assessment of results in this field but as no further investigations have been carried out with stannic chloride as catalyst it must be assumed that the original mechanism proposed for these polymerisations is still valid.

The second class of Friedel Crafts polymerisation proceeds by a polycondensation mechanism. Substituted benzyl monomer may be homopolymerised or copolymerised with other aromatics in the presence of Lewis Acids to produce what are now known as Friedel Crafts polymers.

Several investigations into the mechanism of these polymerisations have been carried out. Parker and Davies[9] have reported a kinetic investigation of the homopolymerisation of benzyl chloride with stannic chloride and concluded that the reaction occurs via a cationic complex of benzyl chloride and stannic chloride. Their results further indicated co-catalysis by water and enhancement of rate in a polar solvent. A detailed kinetic study of the co-polymerisation of di(chloromethyl) benzene with various aromatic co-monomers, has been undertaken by Grassie and co-workers[15-25] and the following mechanism has been deduced



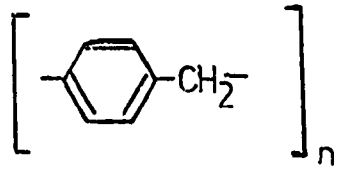
Using a similar system based on $\alpha\alpha'$ dimethoxy-p-xylene Harris[14] has shown that polymers similar to those prepared by Grassie and Meldrum may be obtained by co-polymerisation of this monomer with various aromatics. Again complex formation of the monomer and catalyst is proposed but no kinetic measurements have been made with this system.

In comparison to Friedel Crafts chain polymerisations, considerably less work has been carried out on the polycondensation type of polymerisation although as discussed above, these two modes of polymerisation have many features in common, most notably water co-catalysis, solvent effect on rate and complex formation. In order to obtain more information on the mechanism of this type of polymerisation, further examination of kinetics and products is essential.

1.3 Structure of Friedel Crafts Polymers

Much controversy exists about the structure of products of benzyl polycondensations. Hene and Leicester[34] proposed a polystilbene structure but with little supporting evidence.

The first linear structure was proposed by Jacobson[2], who suggested that the benzene nuclei were predominantly disubstituted in the para position



However, this type of polymer would be expected to be high melting and crystalline.

Flory[35] has suggested that polybenzyl is an example of a polymer exhibiting random branching as illustrated in Figure 1.1. This type of structure would result if at any stage in the reaction, every hydrogen on any benzene nucleus has an equal probability of being substituted subject to the directive influences of the existing substitution.

Based on infrared, oxidative and degradative studies, Haas[5] has presented evidence for a structure consisting of a core of almost completely substituted benzene rings surrounded by a periphery of pendant benzyl groups as shown in Figure 1.2. This structure is supported by Valentine and Winter[6] on the basis of kinetic and spectroscopic evidence.

Although it has been established that polybenzyl is predominantly composed of phenyl and phenylene groups linked by methylene bridges, some doubt still remains concerning the detailed structure. The majority of experimental evidence suggests that the structure proposed by Haas is the true representation but the effect of steric crowding of adjacent benzyl substitutes appears to have been neglected. A more reasonable structure would be one in which the average degree of substitution, in all but the peripheral benzyl groups is lower than that suggested by Haas. Parker[36] has proposed that a more reasonable value for the average degree of substitution is three and has suggested the structure shown on Figure 1.3. In addition he has observed that analytical results for the soluble and insoluble resins are virtually identical and hence deduced that the structures of both types of polybenzyl are similar.

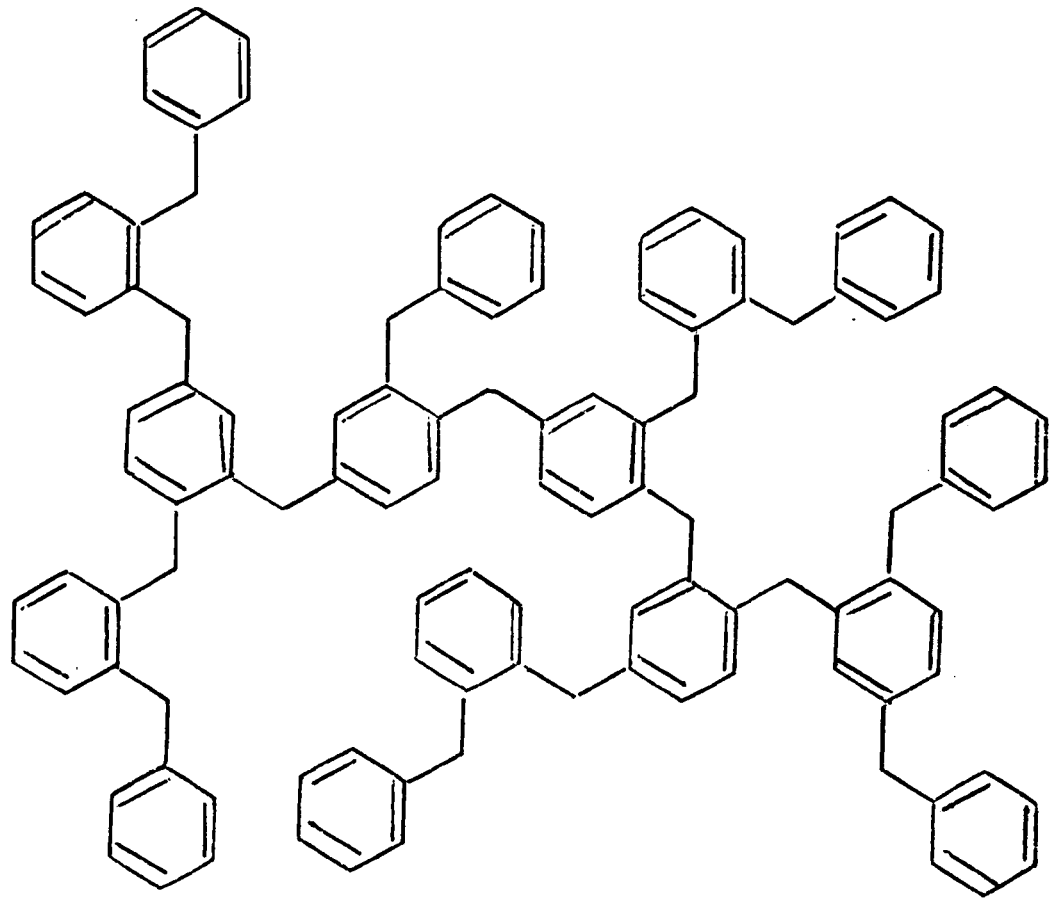


Figure 1.1 - Structure of polybenzyls proposed by Flory

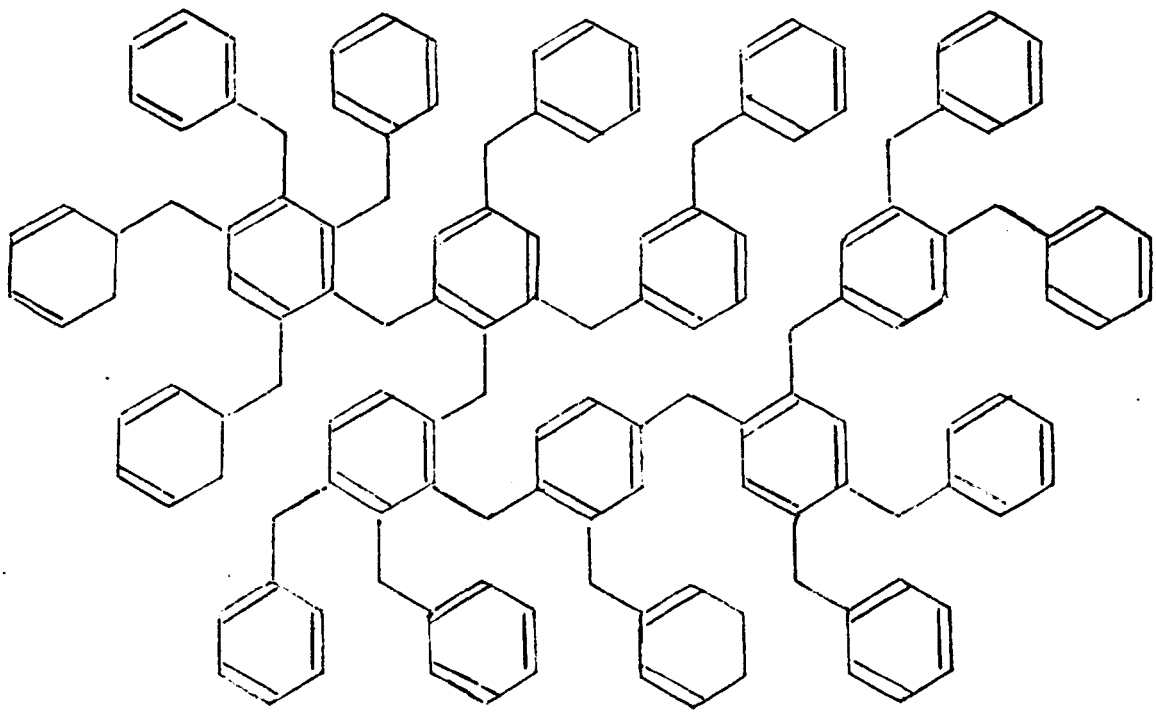


Figure 1.2 - Structure of polybenzyls as proposed by Haas

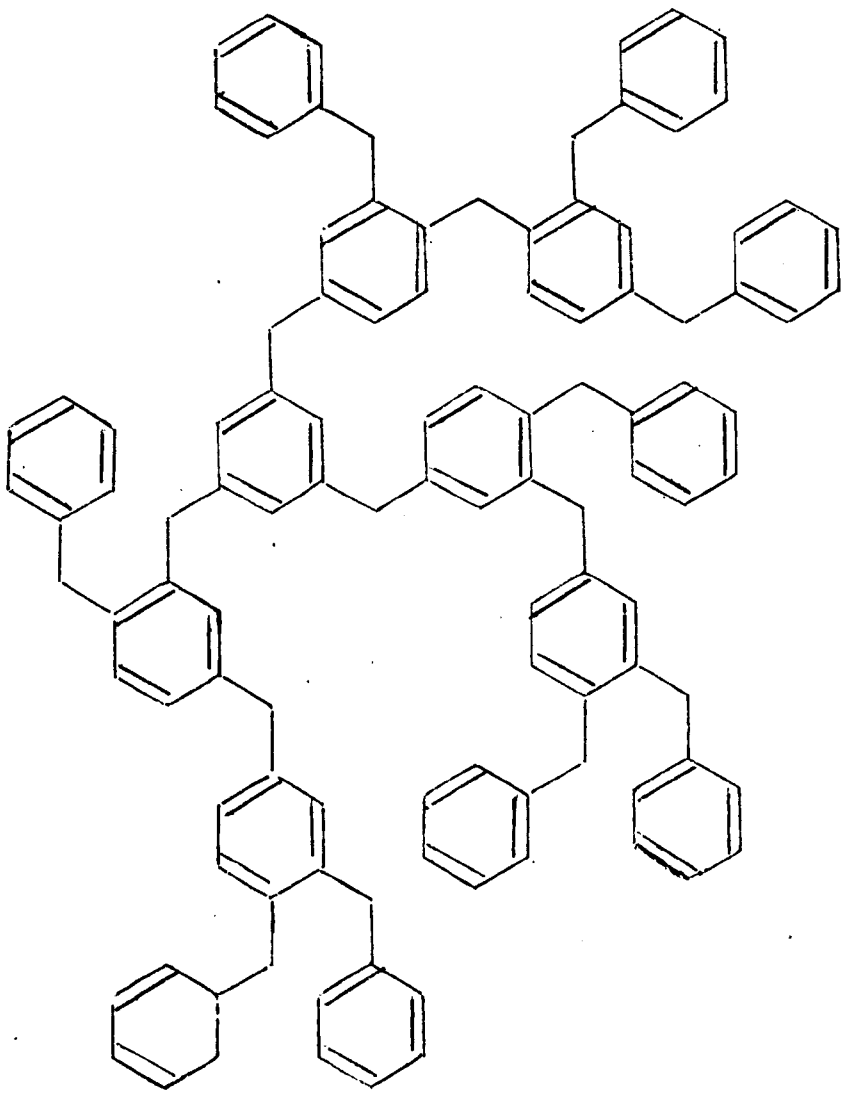


Figure 1.3 - Structure of polybenzyls proposed by Parker

Grassie and Meldrum[15-23] have further demonstrated the versatility of Friedel Crafts Polymers with a detailed investigation of the products and kinetics of the condensation of benzene, diphenyl methane and benzyl chloride with DCMB, using stannic chloride as catalyst. Their results indicate that the frequency of branching in the polymer and hence both its thermal and physical properties can be greatly influenced by varying the aromatic co-monomer. Figure 1.4 illustrates the initial stages of the reaction of a mixture of DCMB and benzene, showing the first five products of condensation which were separated and identified by gel permeation chromatography. The first two products of the reaction must be linear but it has been shown that thereafter branching occurs at the earliest possible stage owing to the greater rate of substitution into the disubstituted aromatic nucleus. This feature has been confirmed by the kinetic measurements of Grassie and Meldrum. It can be seen therefore, that a highly branched structure must be formed preferably in the reaction between DCMB and benzene, leading to a mixture of linear and branched chains in a structure which rapidly increases in complexity.

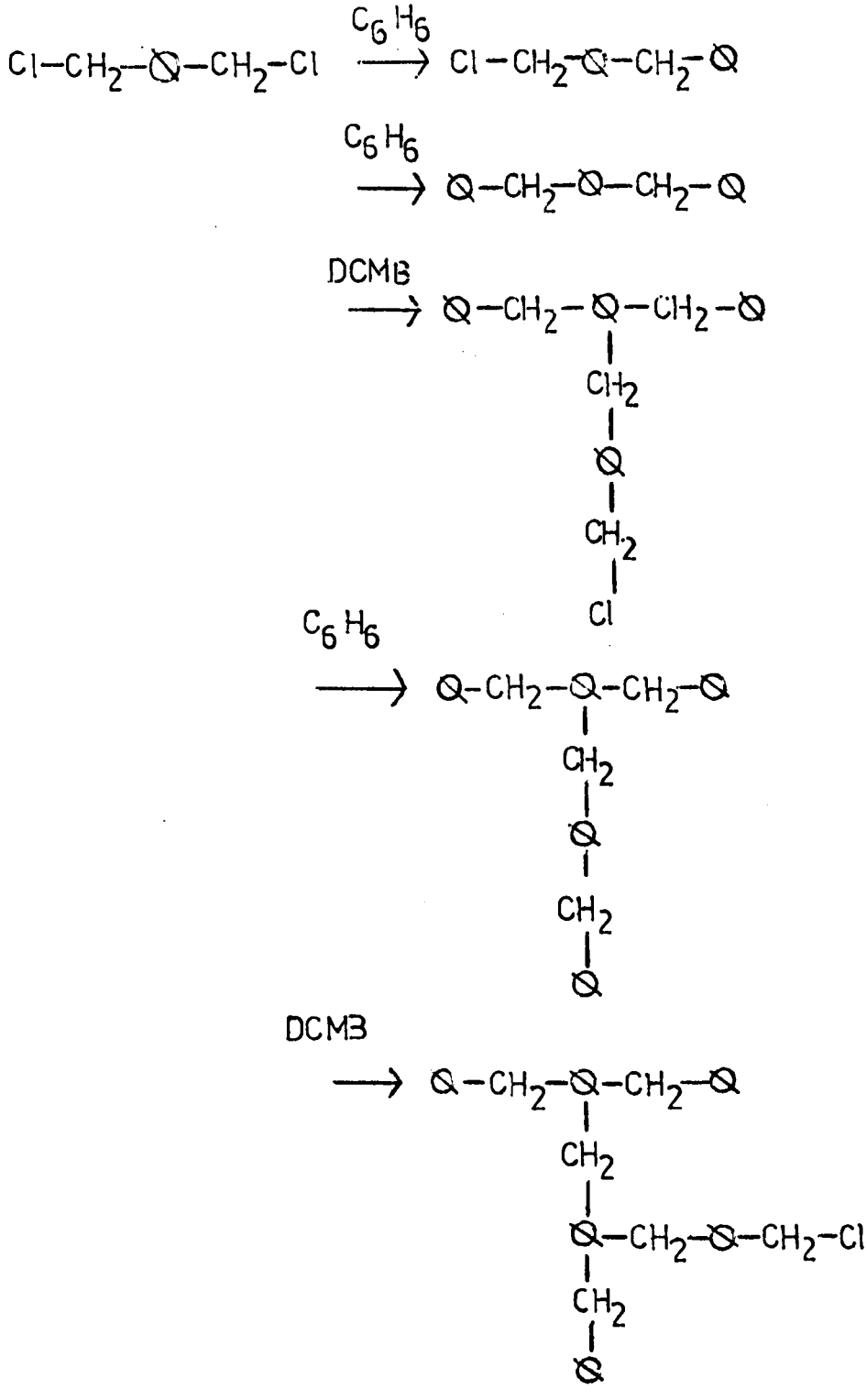
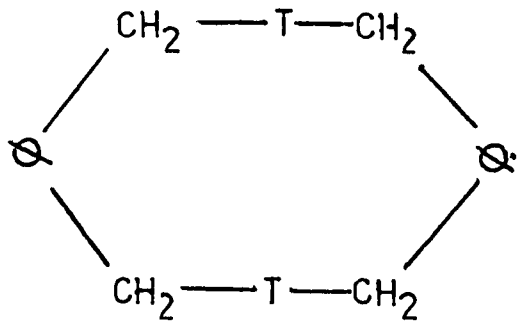


Figure 1.4 - First five stages of DCMB and benzene co-polymerisation

The synthesis of polybenzyls containing heterocycles has also been investigated by Grassie and Meldrum, employing the reaction between aromatic heterocyclic components and DCMB and the thermal properties of these polymers were examined. Their results indicated that the polymers derived from thiophene and DCMB were more stable than the benzene-DCMB counterpart. For this reason Grassie and Colford[24, 25] investigated the products and kinetics of this polymerisation and their observations indicated that the chloromethyl groups react preferentially with the thiophene nuclei so that in the initial stages the products will be less branched than in the DCMB and benzene system. Intramolecular cyclisation has also been shown to occur to produce structures of the type shown below



T- Thiophene

This should result in the formation of a partial ladder structure in the final polymer and accounts for its enhanced thermal stability.

1.4 The Aim of the Current Investigation

As mentioned earlier in this chapter, a greater deal of work has been carried out, in this laboratory, on Friedel Crafts polymers based on DCMB co-polymerised with benzene and thiophene. The results of kinetic investigations of these systems have been correlated with the structures and thermal stabilities of each of the two co-polymers. Although a system based on DCMB has been adapted for industrial use[14] a system based on $\alpha\alpha'$ -dimethoxy-p-xylene (DMPX) as monomer has proved to be more useful. The latter polymerisation is a less endothermic process and involves the liberation of methanol as a condensation product as opposed to hydrogen chloride. Clearly materials based on DMPX are more appropriate for commercial exploitation.

Although the polymers produced by DMPX polymerisation should be similar in many ways to those based on DCMB, it was envisaged that the kinetics of the early stages may follow a different pattern which may lead to structural differences and ultimately to changes in thermal properties. Grassie and Meldrum have made kinetics measurements of the first two stages of DCMB and benzene[16], and have shown that second rate constant is faster than the first by a factor of ten. Using these results they have accounted for early branching which occurs in polymerisation and for the complex nature of the final polymer structure. Harris[14] has shown that pre-polymers based on DMPX cured at a slower rate than those based on DCMB but has not proposed any reasons for these differences.

As DMPX polymers are now commercially available, it was thought worthwhile to undertake a detailed kinetic examination of the first two stages of the co-polymerisation of DMPX with benzene as a first step towards the elucidation of the relationships between structure and stability in this class of polymers so that the factors for the achievement of optimum stability may ultimately be determined. This work is therefore concerned with the kinetics of the first two stages of the co-polymerisation of DMPX and benzene and these results have been correlated with the structural and thermal properties of the polymer and compared with polymers based on DCMB.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 General Precautions

The kinetics of Friedel Crafts reactions are known to be significantly affected by small amounts of water, oxygen and other impurities[29]. For this reason rigorous drying and purification of all materials preceeded all kinetic experiments and polymerisations were carried out under high vacuum (10^{-4} torr). Greaseless PTFE high vacuum stopcocks (Westglass Corporation Ltd.), which have viton 'O' ring seals, were used throughout. The viton 'O' ring seal has been found tc be satisfactory for vacuum work at pressures less than 10^{-5} torr. Greaseless cone and socket joints (Westglass Corporation Ltd.) were also used. The sockets have a polished glass surface and the high vacuum seal (10^{-5} torr) is effected by two viton 'O' rings which are on the polished glass surface of the cone. The use of this apparatus ensured vacuum transfer of all reagents, free of contamination by vacuum grease.

Previous kinetic examination of a similar system employed break seals and all glass apparatus[16]. The use of high vacuum stopcocks however was less time consuming although it necessitated a new design of apparatus.

As noted in Chapter three, stannic chloride catalyses the self-polymerisation of $\alpha\alpha'$ -dimethoxy-p-xylene (DMPX). It was, therefore, necessary to ensure that at no time did these two liquids come into direct contact. The reagents were, therefore, manipulated in a manner such that these two components came together only in high dilution and in the presence of benzene.

2.2 Purification and Drying of Reagents

a) Purification and Drying of $\alpha\alpha'$ dimethoxy-p-xylene

$\alpha\alpha'$-dimethoxy-p-xylene (DMPX). (Albright and Wilson Ltd.) was purified by passing a 100 ml. aliquot through a large basic alumina column (height 1 metre, diameter 5 cm) using diethyl ether as the elutant.

The purified DMPX was then stored, under high vacuum, over freshly ground calcium hydride on a vessel of type (ll) shown in Figure 2.1. Calcium hydride was added via the sidearm and the vessel sealed at the point A. The calcium hydride was removed by filtration through a glass sinter immediately before use. No attempt was made to distill this monomer as the boiling point is greater than 200°C and heating causes re-arrangement to produce explosive products. The effectiveness of this purification procedure was confirmed by gas chromatographic analysis.

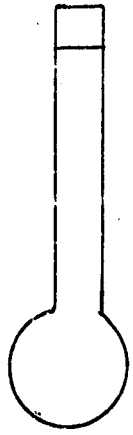
b) Benzene

Benzene (Hopkin and Williams analar grade), which was pre-dried over calcium hydride, was vacuum distilled from a vessel of type (l) (Figure 2.1) into an ampoule of type (ll) containing freshly ground calcium hydride using the greaseless distillation apparatus illustrated in Figure 2.2.

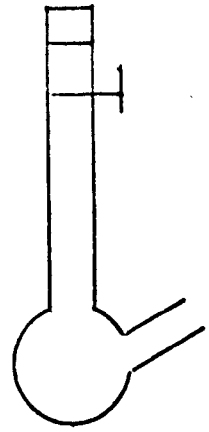
The benzene was stored for one week over calcium hydride after which time, it was transferred to fresh calcium hydride and stored for a further week. The resulting dry benzene was then distilled from calcium hydride to a vessel of type (III) (Figure 2.1) before further distillation to a calibrated ampoule of type (IV). A further distillation from the ampoule transfers the benzene to the reaction apparatus. These three distillations ensure the complete removal of all traces of calcium hydride before polymerisation is carried out.

c) Stannic Chloride

Stannic chloride (BDH reagent grade) was dried using phosphorous pentoxide. Before use phosphorous pentoxide (Hopkin and Williams) was purified by sublimation in the apparatus illustrated in Figure 2.3. It was placed in the small ampoule A which was glass - blown on to the sidearm at B. The resulting apparatus was then evacuated to 10^{-4} torr and the stopcock was closed. The phosphorous pentoxide was then vacuum sublimed by heating with a gas flame and condensed into flask O which was at $-196^{\circ}C$. Finally the apparatus was sealed at the constriction C. Stannic chloride was then distilled onto the freshly sublimed phosphorous pentoxide, employing a similar procedure to that for benzene. The stannic chloride was stored for one week over phosphorous pentoxide, after which time, the above procedure was repeated, transferring the stannic chloride to a fresh batch of sublimed phosphorous pentoxide. After storage for a further week, the stannic chloride was subjected to three more vacuum distillations before reaching the reaction vessel, ensuring that all traces of phosphorous pentoxide had been removed.



(I)



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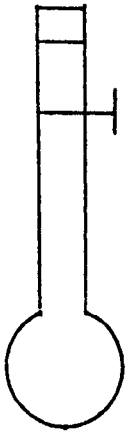


(III)

(IV)

Figure 2.1

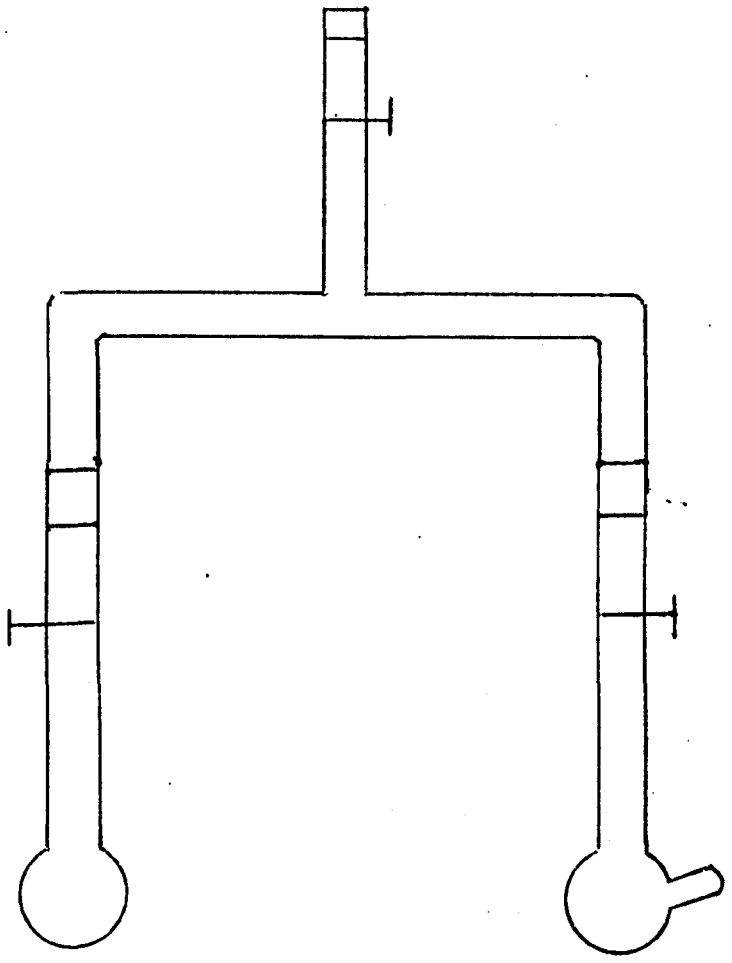


Figure 2.2 - Greaseless transfer apparatus

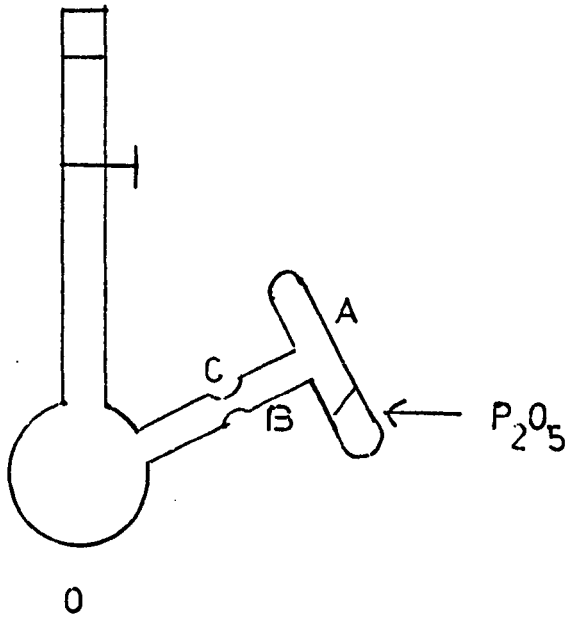


Figure 2.3

d) 1, 2 Dichlorethane (DCE)

1, 2 dichlorethane (BDH reagent grade) was distilled and dried over freshly sublimed phosphorous pentoxide using exactly the same procedure as for stannic chloride.

e) Nitromethane

Nitromethane (BDH reagent grade) was initially purified by vigorous shaking with three aliquots of a solution of sodium bicarbonate and sodium bisulphite. Washing was continued with 5% sulphuric acid, water, sodium bicarbonate and finally again water. It was then pre-dried with anhydrous calcium sulphate before rigorous drying with phosphorous pentoxide using the procedure outlined above, for stannic chloride and 1, 2 dichlorethane.

f) Methanol

Methanol (Hopkin and Williams analar grade) was vacuum distilled into a vessel of type (1) (Figure 2.1), containing sodium metal, using the apparatus illustrated in Figure 2.2. The methanol was allowed to stand in the presence of sodium metal for several minutes before further vacuum distillation to a fresh batch of sodium. The resulting dry methanol was subsequently distilled to an ampoule of type (111) (Figure 2.1) and stored under vacuum.

g) Preparation of Glassware

All glassware was thoroughly cleaned using a cleansing agent, distilled water, analar acetone, and analar chloroform. Before use, it was flamed out at a pressure of 10^{-4} torr to ensure removal of all traces of surface moisture.

2.3 Manipulation of Reagents for Kinetic Experiments

All volatile materials were distilled under vacuum, from their storage ampoules, into calibrated ampoules of the type (IV) shown in Figure 2.1. DCE and nitromethane were distilled into two 100 ml ampoules while stannic chloride and methanol were transferred to 1 ml ampoules, and benzene to a 10 ml container.

For kinetic experiments the apparatus shown in Figure 2.4 was used. The apparatus contains a central flask B of 100 ml capacity into which volatile reagents may be vacuum distilled. The less volatile DMPX could be injected through the rubber septum at A, before distribution of the solution into the reaction bulbs C is effected by inverting the apparatus thereby allowing transfer in a greaseless vacuum system.

The first stage in the procedure was to form the stable stannic chloride methanol complex. This was achieved by distillation of equimolar amounts of methanol and stannic chloride into the central flask B using the apparatus outlined in Figure 2.2. Equilibration from $-196^{\circ}C$ to ambient temperatures allowed the instantaneous reaction of the two liquids to produce a white solid. The required amounts of solvent and benzene were then distilled into the central flask. DMPX which was stored under vacuum over calcium hydride was filtered through a glass sinter and quickly injected into the flask B, through the rubber septum A using a calibrated syringe. The apparatus was inverted, allowing even distribution of the solution to the six reaction bulbs C.

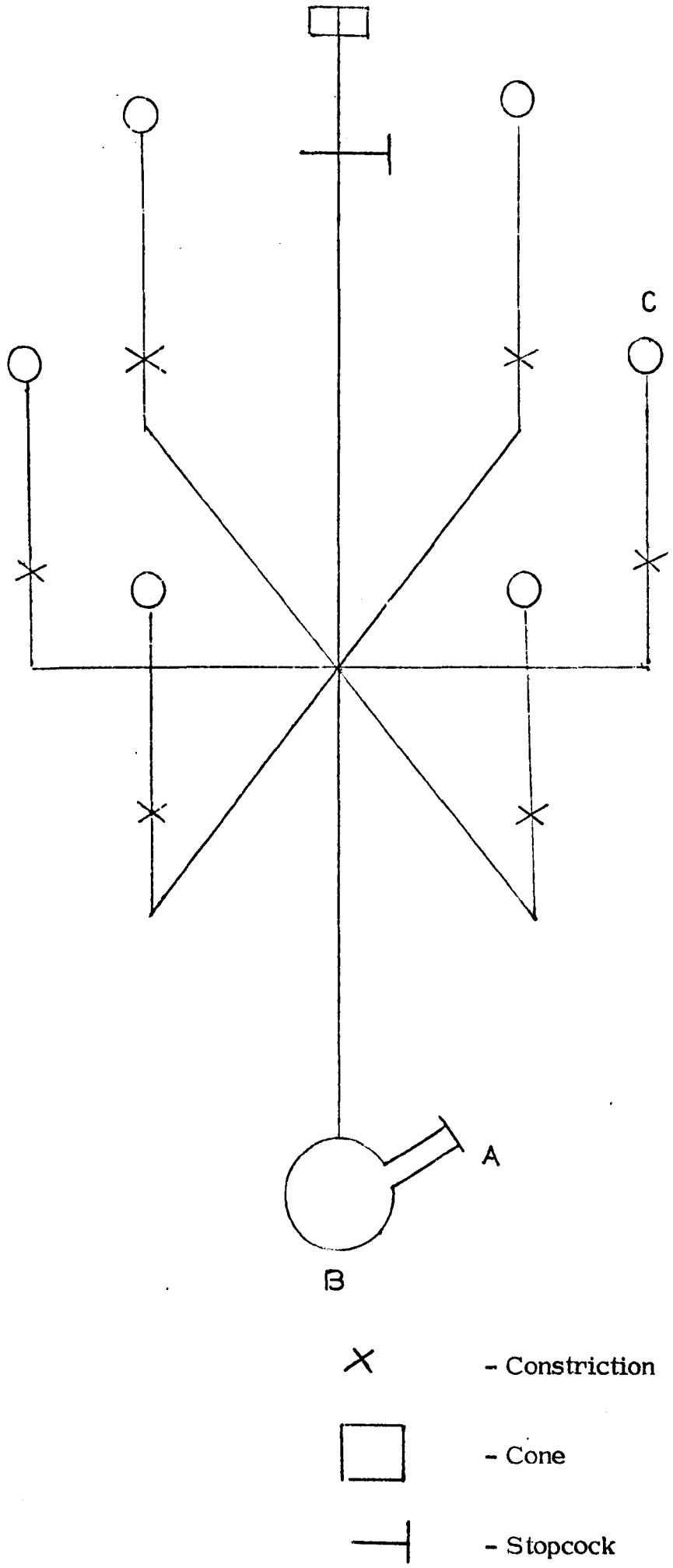


Figure 2.4

The reaction bulbs were quickly immersed in liquid nitrogen at -196°C, before being sealed from the main apparatus and stored at -196°C. The reaction bulbs were placed in the thermostat bath for measured times varying from fifteen minutes to twenty four hours. After the required period, the reaction was quenched by the addition of 5 ml of distilled water. The organic layer was then separated from the aqueous layer and dried over anhydrous sodium sulphate. The solution was now ready for G.L.C. or G.P.C. analyses.

2.4 Polymerisation

Polymerisations were carried out under vacuum in a thermostat bath (Townsen and Mercer) at 30 and 50°C. Polymers of higher molecular weight were produced under a nitrogen atmosphere at solvent reflux temperatures.

2.5 Polymer Recovery and Purification

a) Soluble Polymers

After washing the solution with water the polymer was precipitated by the slow addition of the solution to three litres of analar methanol with constant stirring. The resulting polymer was twice reprecipitated from chloroform solution and finally dried in a vacuum oven at 100°C for 48 hours.

b) Insoluble Polymers

The insoluble polymers were filtered from the reaction mixture. They were purified by washing with distilled water, acetone, chloroform and finally diethyl ether. After each washing the product was dried in a vacuum oven at room temperature and after the final washing, it was dried in a vacuum oven at 100°C

2.6 Techniques for Chromatographic, Spectroscopic and Thermal Analysis

a) Gas Liquid Chromatography (G.L.C.)

Quantitative G .L.C. analyses were carried out using a Microtek 2000 R gas chromatograph, equipped with dual columns, flame ionisation detector and a linear temperature programmer . As described in Chapter four, calibration of the detector was carried out for DMPX and the first two reaction products using toluene as internal standard. In order to achieve a good separation, samples were injected into a 1% silicone gum (SE 30) on 100/120 embacel column which was then linearly programmed from room temperature to 250^{o}C.

b) Thin Layer Chromatography (T.L.C.)

Small amounts of the first two products, required for G.L.C. detector calibration, were first isolated by the use of large scale preparative thin layer chromatography (T.L.C.). This technique is less time consuming than preparative G.L.C. and its simplicity is an added advantage. Chromatoplates were prepared by the method of Stahl.[39]

c) Gel Permeation Chromatography (G.P.C.)

G.P.C. analyses of high and low molecular weight products were carried out using a Waters G.P.C. instrument (University of Strathclyde) equipped with a solvent pump and separated products were detected by monitoring changes in refractive index. Molecular weight determination as well as product analysis[38] could be obtained by this technique.

d) Gas Chromatography - Mass Spectrometry (G.C.M.S.)

Reaction products which could be separated by G.L.C. were initially analysed by means of an LKB 900 (LKB Produkter) combined gas chromatograph - mass spectrometer allowing mass spectrographs of individual products to be obtained.

e) Mass Spectrometry

The mass spectra of isolated reaction products were obtained using an AEI MS12 mass spectrometer using ionisation voltages within the range 20 e.v. - 70 e.v.

f) Infrared Spectroscopy

Infrared spectra were obtained using a Perkin Elmer 257 spectrometer. Samples were prepared as potassium bromide discs or run as liquid films on sodium chloride discs.

g) Nuclear Magnetic Resonance (NMR)

The NMR spectra of polymers and low molecular weight reaction products were obtained using a C60 HL Jeol High Resolution NMR spectrometer (60 MHZ). Deuterated chloroform was used as a solvent in most cases.

h) Thermogravimetric Analysis (T.G.A.)

T.G.A. was carried out using a Du Pont 950 Thermal Gravimetric Analysor. The sample was heated at a rate 10^{o}C per minute in a dynamic nitrogen atmosphere to 800^{o}C. Thermogravimetric analyses were also carried out under vacuum using a Cahn Thermobalance which was linked to T.V.A. apparatus described below.

i) Thermal Volatilisation Analysis (T.V.A.)

Since T.V.A. has been the subject of numerous publications[40-44] and is now well established as a technique of thermal analysis, only a brief description is given here.

T.V.A. involves the programmed heating of a polymer under vacuum. The volatile products are divided into four parts which pass along equivalent routes incorporating cold traps at four different temperatures, 0^{o}, -45^{o}, -75^{o}, -100^{o}C. Pirani gauges are situated after each cold trap and a fifth gauge follows the main liquid nitrogen trap at -196^{o}C. The pirani response is monitored on a multichannel pen recorder together with the output from the oven thermocouple. The T.V.A. traces thus give a measure of pressures of the volatile products at the various trap temperatures. The less volatile degradation products are collected on the water cooled 'cold ring' surface of the glass degradation tube and more volatile products may be collected for analysis in a -196^{o}C trap at the end of the system.

2.7 Synthesis of Di-(benzyl) Benzene

Since dibenzyl benzene, which is the second product of the DMPX and benzene reaction could not be obtained from commercial sources, a method of synthesis of this compound was devised as only limited amounts could be obtained by chromatographic separation.

Friedel Crafts alkylation reactions strongly activate further ring substitution while the corresponding acylation reaction results in a reversal of this effect. For this reason, dibenzoyl benzene was first produced, by acylation, and dibenzyl benzene obtained by subsequent reduction.

1, 4 terephthalyl dichloride was obtained by heating a mixture of phosphorous pentachloride and terephthalic acid at 110°C, without solvent, for three hours. Dibenzoyl benzene was then produced by the method of Munchsmeyer as follows:[45]

Terephthalyl chloride (5g) was dissolved in benzene (120 ml) before the addition of aluminium chloride (7g) and the solution refluxed until evolution of hydrogen chloride had ceased. The solution was then washed with water and excess benzene removed, to give dibenzoyl benzene (6g 70%). Recrystallisation was from cold ethanol, MP 161°C (Lit MP 161°C from ethanol).

Dibenzoyl benzene (5g) was dissolved in digal (100 ml) before hydrazine hydrate (5 ml) was added. Potassium hydroxide (2.5 g) was added and the mixture stirred at 80°C for one hour before the reflux condenser was removed and the mixture temperature was raised to 175°C for twenty minutes. The reaction mixtures was poured into water, extracted with ether, washed, dried and solvent removed to give the crude product. Crystallisation from ethanol gave the pure dibenzyl benzene (4.1 g/88%) MP 85-86°C (Lit MP 86°C) (NM R 2.7 τ 2.8 τ 6.1 τ).

CHAPTER 3

GENERAL OBSERVATIONS AND FACTORS AFFECTING POLYMERISATION KINETICS

3.1 Introduction

Prior to undertaking a detailed kinetic examination of co-polymerisation of $\alpha\alpha'$ dimethoxy-p-xylene (DMPX) and benzene, a series of preliminary investigations were carried out in order to establish the most favourable conditions of kinetic studies and to investigate the various parameters which affect reaction kinetics.

This chapter describes the various complex features of DMPX and benzene co-polymerisation and their effect on polymerisation kinetics and compares these observations with those found for a corresponding co-polymerisation, based on di(chloromethyl) benzene (DCMB) which has been extensively investigated by Grassie and Meldrum[16]. The approach to kinetics, described in chapter four, is based on these initial findings.

3.2 General Observations

In co-polymerisations of DCMB and benzene, catalysed by stannic chloride, in 1, 2 dichlorethane solvent, the following observations were made:- The solution, which was initially clear, rapidly developed a yellow colouration which slowly deepened to a dark red before insoluble polymeric material was observed to precipitate from the reaction solution. Colour was rapidly discharged upon quenching the polymerisation by the addition of water.

Under similar conditions (Table 3.1) but using DMPX instead of DCMB as monomer, contrasting effects were observed. A white suspension was immediately produced on the addition of stannic chloride to the reaction solution and was observed to persist throughout the early stages of reaction before giving way to a yellow coloured transparent solution. Under these conditions (Table 3.1), no gelation or precipitation of insoluble polymer was observed in the course of DMPX reaction. Attempts to precipitate soluble polymer from the reaction solution were also unsuccessful. However at higher temperatures, using higher concentrations of stannic chloride, small amounts of insoluble polymer could be produced (Table 3.2). The bulk of high molecular weight material produced under these conditions was soluble in the reaction solvent and was precipitated using methanol as a non solvent. The resulting polymer was found to be soluble in aromatic and halogen containing solvents. These observations are in contrast with DCMB polymerisations which produced largely insoluble polymers.

TABLE 3.1

Monomer	Monomer Concentration (moles/litre)	Benzene Concentration (moles/litre)	Stannic Chloride Concentration (moles/litre)	Temperature (^{o}C)	Time (hours)
DMPX	0.12	1.34	0.016	50	3
DCMB	0.14	1.36	0.016	50	3

TABLE 3.2

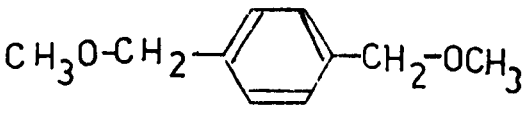
Concentration of DMPX (moles/litre)	Benzene Concentration (moles/litre)	Stannic Chloride Concentration	Temperature °C	Time (hours)
0.12	1.34	0.11	70	24

The suspension noted in the DMPX polymerisations, persisted throughout the range of solvents used in this investigation. Methylene chloride, carbon tetrachloride and 'ethanol free' chloroform all produced effects similar to 1, 2 dichlorethane. Highly polar solvents such as nitromethane and nitrobenzene also failed to produce a homogeneous solution in the initial stages but the suspension persisted for much shorter times than in non polar solvents.

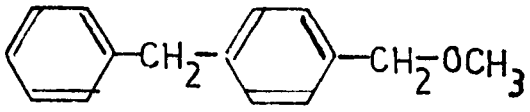
3.3 Complexes of Stannic Chloride and Inhibition by Methanol

The formation of stable complexes of metal halides and oxygen containing compounds such as ethers and epoxides is well known[46]. Their formation is attributed to the strong co-ordinating power of the oxygen lone pair of elections to the central metal atom of the halide. The white suspension, apparent in DMPX polymerisations, is formed by reaction of DMPX and stannic chloride in solution and it appears likely that co-ordination of one or two of the diether oxygen lone pairs to the tin nucleus occurs to produce a highly polar insoluble complex. Complexes of this nature are known to be extremely hygroscopic and air sensitive, and these factors, together with the insolubility problems, prevented detailed spectroscopic analysis of this adduct. Analysis for tin as tin dioxide revealed the stiochometry of the complex to be 1:1 (DMPX: $SnCl_4$). (Found 27.3% Sn; theoretical for 1:1 complex of $SnCl_4$: DMPX 27.8% Sn)[47].

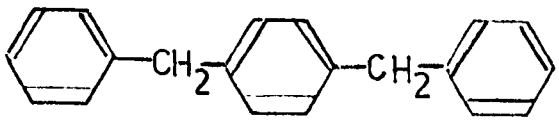
G.L.C. analysis of the reaction mixture of the early stages of the polymerisation of DMPX and benzene, where the insoluble complex is evident, revealed the presence of DMPX (1) and structures (11) and (111) shown below.



(1)

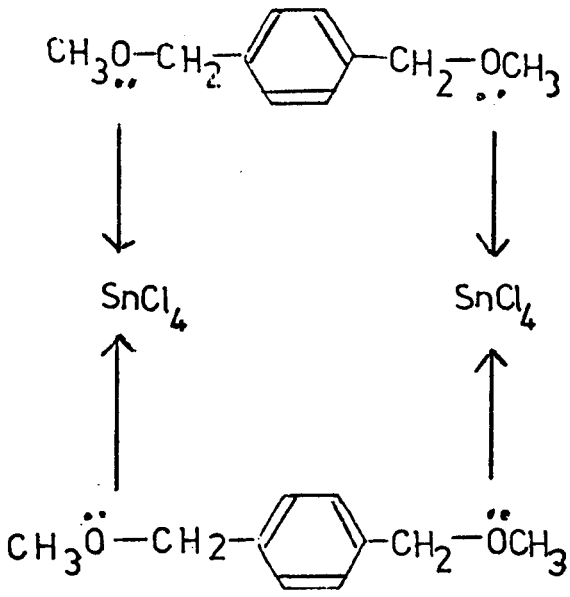


(II)



(III)

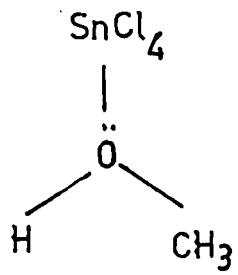
Identification of these structures was carried out as described in chapter five. Structure (11) arises from condensation of DMPX and benzene and (111) from condensation of benzene with (11). From the findings, it is clear that the complex is a precursor of the two reaction products and condensation has occurred involving both methoxyl groups of the diether, it is also evident that both oxygen lone pairs can be involved in co-ordination. A monomeric structure where both oxygen atoms are co-ordinated is sterically unattractive but a dimeric structure, such as (IV) shown below incorporates both oxygen atoms and is sterically feasible.



(IV)

As previously mentioned, condensation of DMPX and benzene occurs to produce (II) which by further condensation produces (III) and finally polymer. Condensation of this nature would produce methanol as a by-product and the effect of this on polymerisation must be carefully examined. Alcohols are known to form complexes with Lewis acids such as stannic chloride[46]. A complex of 1:1 stiochometry of methanol and stannic chloride has been isolated by Pfeiffer[48] and complexes of metal halides and methanol, which are richer in methanol, are known to exist[49]. It was anticipated that complexing of this nature would occur in the course of DMPX polymerisations and that this feature would result in complications in the kinetics of the reaction. For these reasons, the effects of addition of methanol to stannic chloride were examined. As described in chapter two, mixing of dry methanol and stannic chloride, under vacuum

in equimolar proportions, resulted in the instantaneous appearance of a white solid and total consumption of each of the starting materials. Tests were carried out using infrared spectroscopy, for the presence of hydrogen chloride as a reaction product, under vacuum conditions. However the resulting spectrum did not show the characteristic P Q and R infrared fine structure around 3000 cm^{-1} which is characteristic of hydrogen chloride. This indicated that complex formation was the result of addition rather than substitution of the chlorine atom in stannic chloride. Two addition structures seem possible; in structure (V), the methanol oxygen acts as a donor atom to the tin nucleus, while structure (VI) is an ionic structure similar to that which is formed from equimolar amounts of water and stannic chloride[29].



(V)

$H^{(+)}SnCl_4OCH_3^{(-)}$

(VI)

The stannic chloride - methanol complex was found to be soluble in water and in a range of organic solvents, including 1, 2 dichlorethane and nitromethane. Solubility was not apparent in less polar solvents such as benzene and solubility was noted to be greater in solvents of high polarity. Co-ordinated complexes, similar to structure (V) are insoluble in water and in most organic solvents and for this reason structure (V) seems unlikely. As will be discussed later, the stannic chloride - methanol complex is active as a Friedel Crafts catalyst and this property together with the solubility evidence would tend to suggest that an ionic structure such as (VI) is more likely. Further evidence for the ionic nature of this complex comes to light in the kinetic analysis of a system which employs this catalyst, described in chapter four.

Methanol and other alcohols are known inhibitors of Friedel Crafts polymerisations [50, 51]. An examination of the effects of the addition of small amounts of methanol on the initial rate of polymerisation was therefore necessary before any meaningful kinetic experiments could be carried out. Table 3.3 and Figure 3.1 summarise the results of these experiments. At this point, it is worth noting that no initial heterogeneity is evident after sufficient amounts of methanol had been added to form the soluble 1:1 methanol - stannic chloride complex. From the quantitative information obtained from these experiments, it is clear that the initial rate of polymerisation decreases with increasing methanol concentration. When the molar ratio of methanol to stannic chloride is unity, the reaction rate is still appreciable but as this ratio approaches two, the reaction rate diminishes towards zero.

As methanol is produced by condensation co-polymerisation of benzene and DMPX, it was envisaged that autoinhibition would occur. This was confirmed by preliminary kinetic experiments. Quantitative estimations of the reaction rate were obtained using G.L.C. as outlined in chapter four. An efficient separation of compounds (I), (II), and (III) was obtained and the use of toluene as an internal standard permitted determinations of the absolute concentrations of each component at any time. The theoretical amounts of methanol, produced, were calculated by assuming that one mole of methanol is produced for every mole of (II) which is formed and two moles of methanol for every mole of (III) which is formed. As will be shown later, reaction beyond the first two products, under these conditions is small and any additional methanol formed by further reaction maybe neglected. The calculated amounts of methanol together with experimentally determined concentrations of (I), (II) and (III) are listed in Table 3.4 while figure 3.2 illustrates the disappearance of (I) with time.

TABLE 3.3

$SnCl_4$ moles/litre	CH_3OH moles/litre	Initial Rate of disappearance of (moles/litre/sec.)
4.4×10^{-2}	0	1.85×10^{-5}
4.4×10^{-2}	4.4×10^{-2}	1.50×10^{-5}
4.4×10^{-2}	8.8×10^{-2}	3.2×10^{-7}

Initial concentration of = 1.2×10^{-1} moles/litre

Temperature = 50°C

TABLE 3.4

Time (Minutes)	l moles/litre x 10	ll moles/litre x 10^2	lll moles/litre x 10^2	CH_3OH moles/litre x 10^2	Ratio of CH_3OH to $SnCl_4$	$\frac{d(1)}{dt}$ moles/litre/sec x 10^5
0	1.2	0	0			1.85
15	1.01	1.80	0.30	2.40		
30	0.86	2.20	1.26	4.72	1.07	0.85
45	0.78	2.31	2.06	6.43		
90	0.75	2.30	2.20	6.70		
200	0.70	2.60	2.58	7.66		
240	0.68	2.70	2.70	8.1	1.80	0.09

Temperature = 50°C

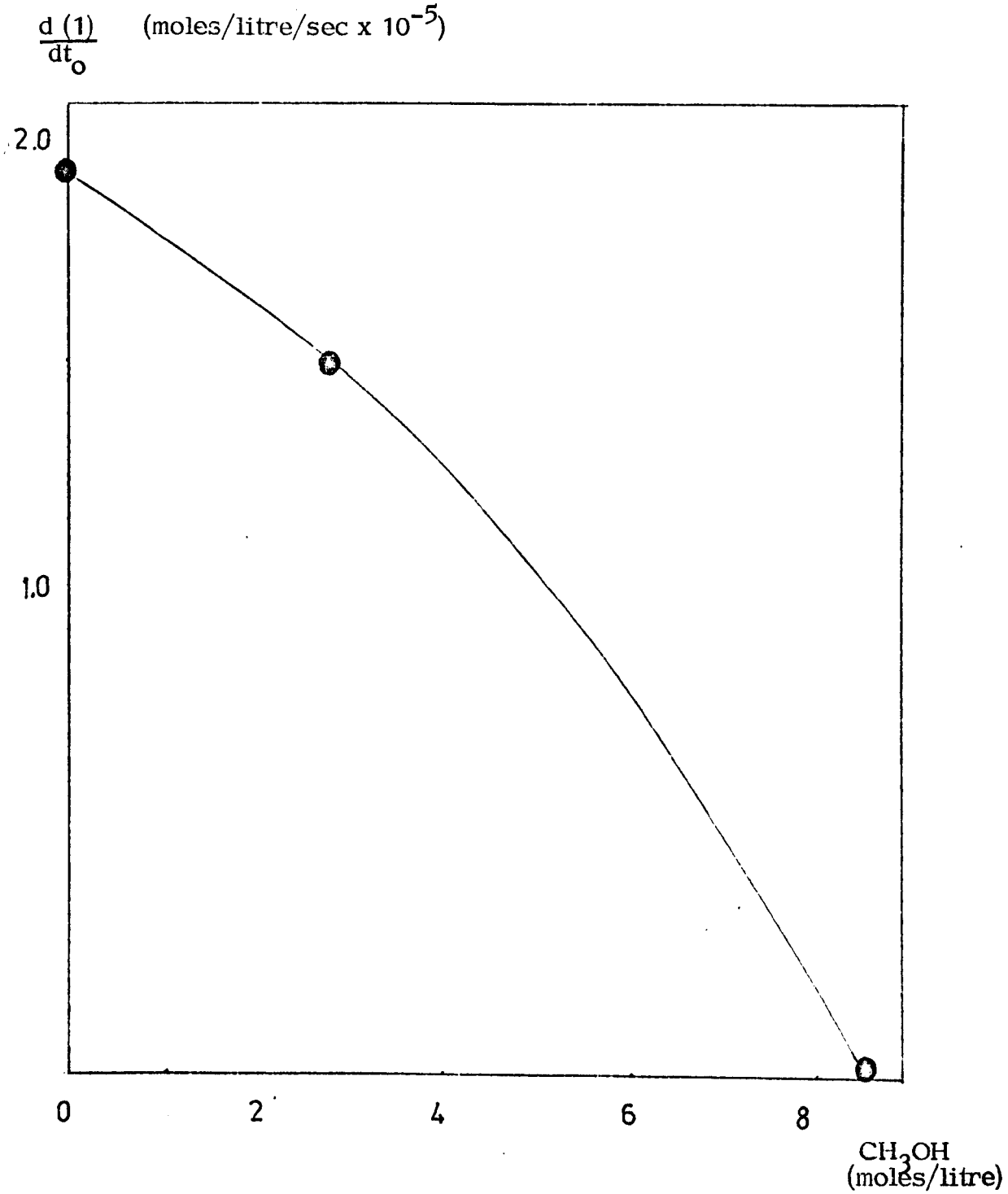

$\frac{d(1)}{dt_o}$ (moles/litre/sec x 10^{-5})
2.0
1.0
0
2
4
6
8
CH_3OH
(moles/litre)

Figure 3.1

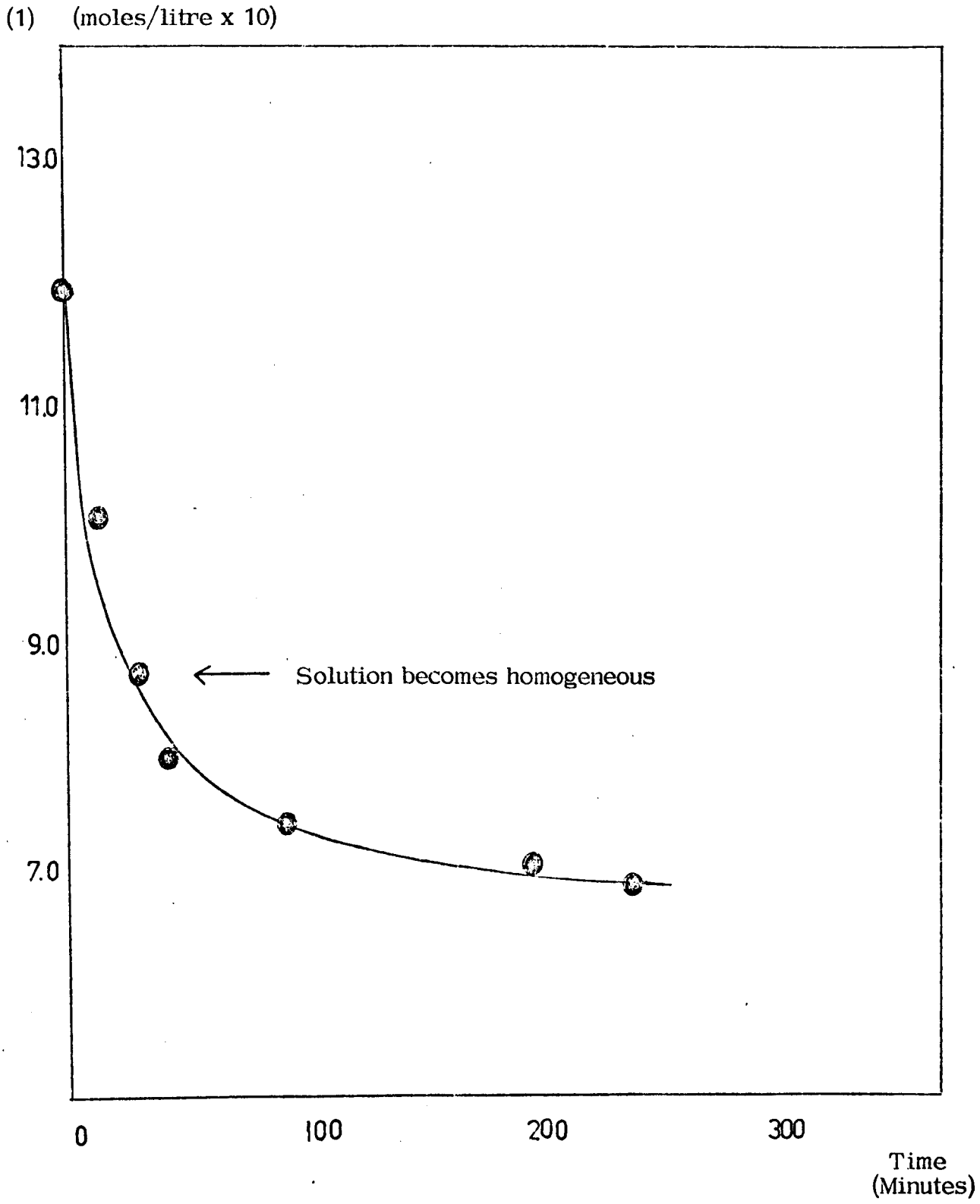

(1) (moles/litre x 10)
13.0
11.0
9.0
7.0
Solution becomes homogeneous
0
100
200
300
Time
(Minutes)

Figure 3.2

As previously stated, the reaction media is heterogeneous in the initial stages. As shown in the graph (Figure 3.2), solution is effected after thirty minutes reaction, at which point the molar ratio of the calculated concentration of methanol to the initial concentration of stannic chloride is close to unity (0.044M $SnCl_4$: 0.047M CH_3OH). It is therefore proposed that, at this point, the soluble stannic chloride-methanol complex is formed in preference to the insoluble DMPX - stannic chloride complex, resulting in a completely homogeneous solution. It is also clear that the reaction rate becomes very small as the molar ratio of methanol to stannic chloride approaches two. When the molar ratio is one, the rate of reaction is of the same order of magnitude as the initial rate which is observed when equimolar proportions of methanol and stannic chloride are added in the initial reaction mixture. These results are therefore consistent with those of the experiments where methanol is added to the initial reaction mixture.

Analysis of the reaction mixture, by G.L.C. revealed the presence of only benzene, solvent and components (I), (II) and (III), indicating that methanol was consumed by the catalyst. However, previous workers[14] have reported the evolution of methanol in the course of DMPX polymerisation but their work was carried out at higher temperatures ($> 100^{\circ}C$) and it is proposed that complexes of methanol and stannic chloride decompose, evolving methanol, at these high temperatures.

3.4 Extent of Polymerisation

Gel permeation chromatography (GPC) was employed, as a means of investigating the extent of reaction beyond the first two products. Analysis by G.L.C. is restricted to the first two reaction products, owing to the involatility of the later products but GPC is capable of separating components of higher molecular weight, although separation is

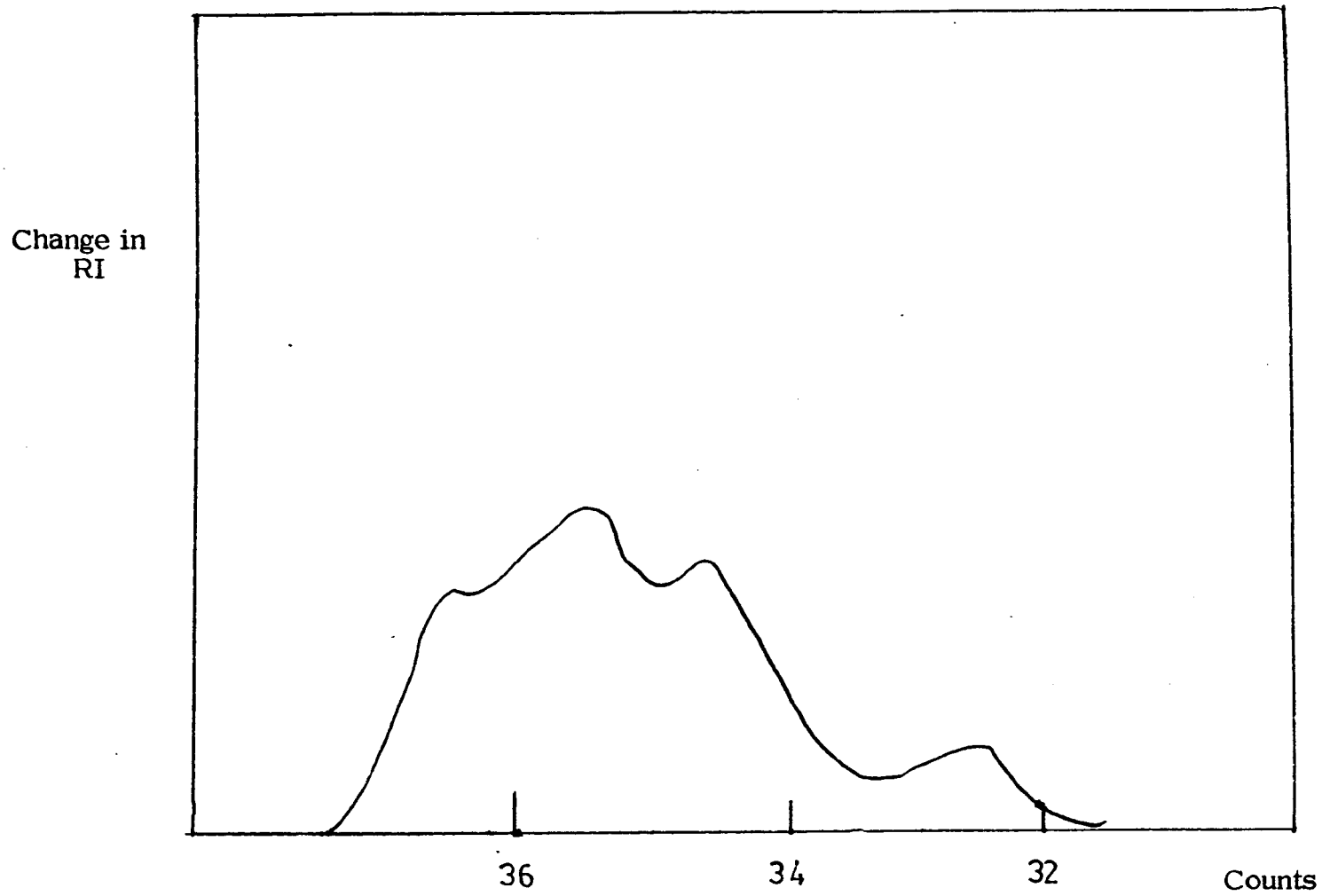


Figure 3.3

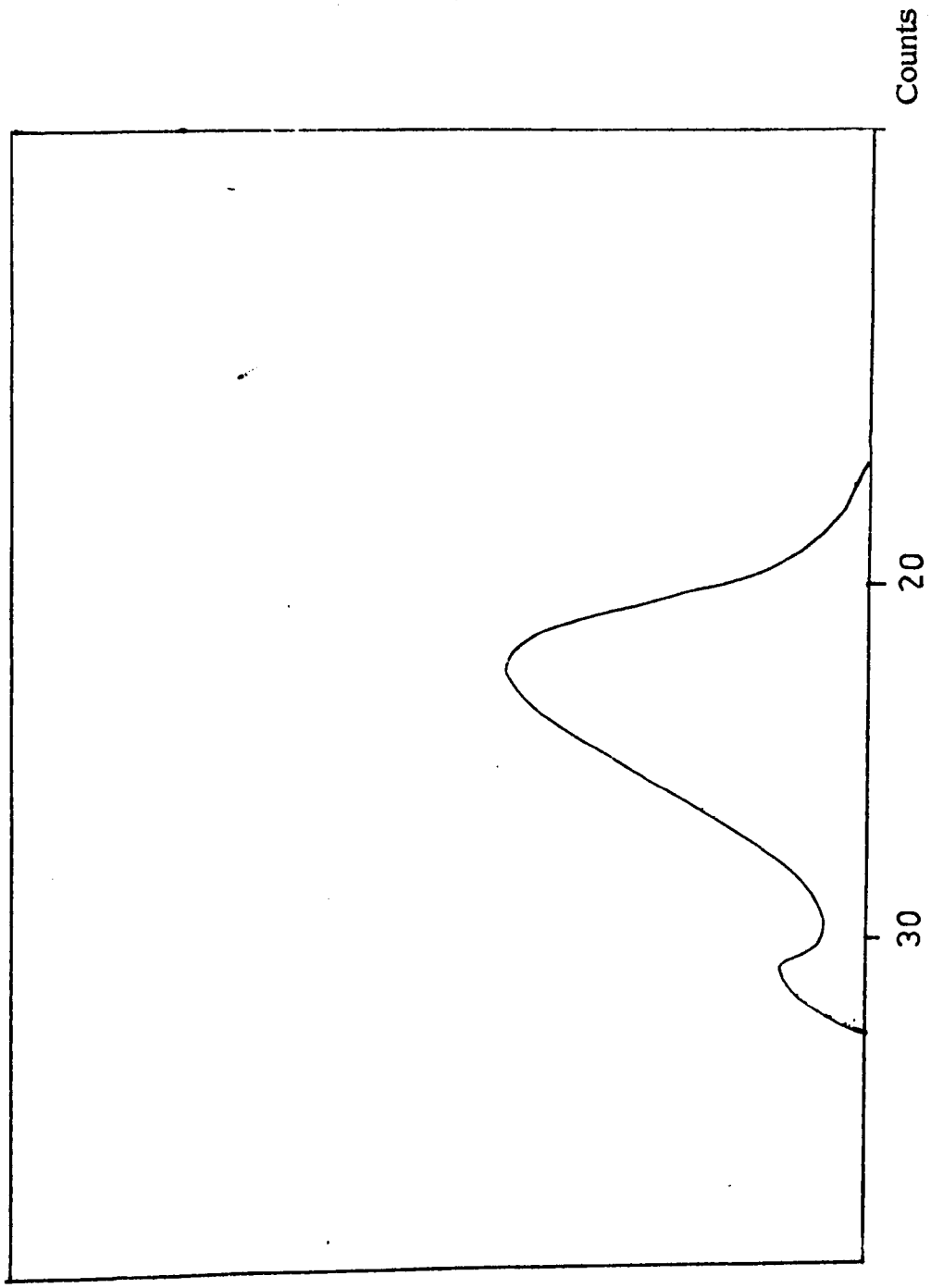


Figure 3.4

TABLE 3.5 (a)

Peak	Retention Value (Counts)	Approximate Molecular Weight (From calibration curve)
a	36.5	180
b	35.5	230
c	34.5	280
d	32.5	400

TABLE 3.5 (b)

Count Values for Pure Samples of (I) (II) (III)

Peak	Retention Value (Counts)	Molecular Weight
(I)	36.5	166
(II)	35.5	212
(III)	34.5	258

less efficient. GPC analysis was carried out on a solution obtained from three hours of reaction under the conditions listed in Table 3.4. (G.L.C. analysis of this mixture has shown conversion to be of the order of 40%). Analysis was also made of polymers precipitated in methanol from reaction under more extreme conditions, at higher temperatures and higher concentrations of stannic chloride as listed in Table 3.2. The trace obtained for 40% conversion is shown in Figure 3.2 and the information obtained is summarised in Table 3.5. Traces were obtained from pure samples of (I), (II) and (III) and by comparison of retention times, the peaks in the traces of the mixtures were identified. From GPC analysis, it is clear that no high molecular weight material is obtained after three hours reaction under the conditions listed in Table 3.4. However, analysis of polymerisation mixtures after twenty four hours reaction using conditions outlined in Table 3.2., molecular weights of as high as 17,000 may be obtained (Figure 3.4).

3.5 Effect of Solvent

The relationship between the rate of polymerisations catalysed by Lewis acids and the dielectric constant of the reaction media has been the subject of numerous publications [29, 46]. It has been demonstrated that the rate of reaction increases as the dielectric constant of the solvent is increased although no direct mathematical relationship between these two factors has been formulated. As this investigation involves the use of benzene, 1, 2 dichlorethane and nitromethane, it was thought necessary to examine the effect of the dielectric constant on the rate of DMPX based polymerisation. The rate of reaction was examined in pure benzene, 1, 2 dichlorethane and in nitromethane. In the latter two cases the concentration of benzene, DMPX and stannic chloride - methanol complex was kept constant for each experiment, in order that the rates of reaction

in the two solvents could be compared directly. In the case of the reaction on pure benzene, the concentrations of DMPX and stannic chloride are equal to those used for the other two kinetic experiments. A 1:1 methanol-stannic chloride complex was used as a catalyst and with pure benzene, the media is heterogeneous.

Table 3.6 illustrates the results of these experiments. The dielectric constants were obtained from a previously published plot of mole fraction of benzene in solvent against a measured dielectric constant [52, 53]. These results clearly indicate that the rate of reaction is considerably affected by a change in solvent dielectric. The rate of reaction in benzene, is slower by a factor of one hundred than in 1, 2 dichlorethane, while reaction in nitromethane enhances the reaction rate by a factor of thirty.

It was therefore concluded that in all experiments the concentration of benzene should be kept constant to avoid variation in dielectric constant leading to subsequent complications in kinetic analysis.

3.6 Effect of Homopolymerisation

As illustrated in Figure 3.5, a mechanism whereby DMPX maybe homopolymerised in the presence of stannic chloride is possible. Competition of this reaction with co-polymerisation would lead to complications in kinetic analysis. For this reason, the homopolymerisation of DMPX was investigated using concentrations of DMPX and stannic chloride as given in Table 3.4. GLC analysis, after three hours reaction, revealed the presence of DMPX and two further peaks (II)a and (III) a. These two peaks are undoubtedly due to the presence of the first two products of homopolymerisation. However these two peaks are absent from all traces

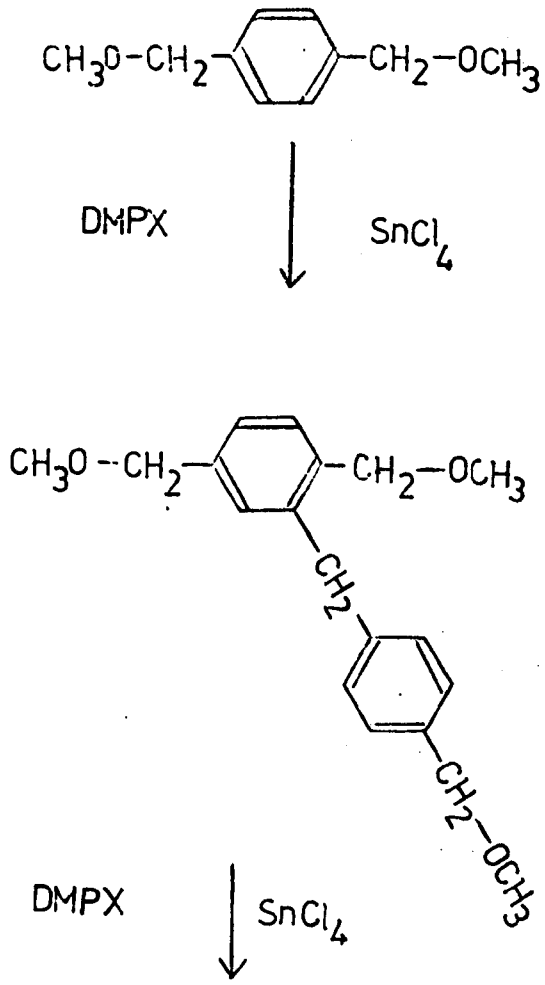
TABLE 3.6

Solvent	Dielectric Constant	$\frac{d(1)_o}{dt}$ moles/litre/sec
Nitromethane and benzene	37.0	5.6×10^{-6}
1, 2 dichlorethane and benzene	8.0	2.0×10^{-7}
Pure benzene	2.3	1.5×10^{-9}

$(1)_o = 0.06M$

$(SnCl_4\ CH_3OH)_o = 0.044M$

$(Benzene)_o = 1.13M$



HOMOPOLYMER

Figure 3.5

obtained from solutions from co-polymerisation in a high excess of benzene (molar ratio 10:1). It appears that with a high concentration of benzene, the co-polymerisation reaction occurs preferentially and that hompolymerisation, under these conditions is negligible.

Further evidence for the absence of homopolymerisation is cited in Chapter five, (where NMR spectral measurements have demonstrated the absence of methoxyl groups in the co-polymer and their presence in considerable concentration in the homopolymer.

3.7 Co-catalysis by Water

The need for a proton containing co-catalyst, in reactions of this type, has been demonstrated on numerous occasions [54, 55]. However, Parker and Davies [9] have shown that polymerisation of benzyl chloride will occur under rigorous anhydrous conditions. Grassie and Meldrum[16] have also demonstrated that the co-polymerisation of benzene with DCMB proceeds in the absence of water using stannic chloride as catalyst[16]. This reaction is however co-catalysed by water in small concentrations and inhibited by larger concentrations; a maximum rate of polymerisation is observed when the molar rate of stannic chloride to water is unity. This observation was attributed to the formation of a 1:1 stannic chloride - water adduct which has greater catalytic activity than free stannic chloride. The inhibition noted at higher water concentrations is thought to result from the formation of complexes, richer in water, which are less active.

In the present investigation, it has been shown that co-polymerisation of benzene and DMPX is possible in the absence of water. For the reasons outlined above, it was decided that reproducible results, in kinetic analysis, could only be obtained using absolute anhydrous conditions. A full account of how this was achieved is presented in the preceeding chapter.

3.8 Discussion

From general observations and quantitative measurements obtained, it is clear that the mechanism of polymerisation involving DMPX deviates considerably from the established mechanism of the reaction involving DCMB. It is also apparent that DMPX produces polymers of greater solubility than those based on DCMB.

The formation of an insoluble complex of DMPX and stannic chloride contrasts with the situation in the DCMB polymerisation which is homogeneous throughout. It has been proposed by Grassie and Meldrum[16] that a reversible reaction of stannic chloride and DCMB produces a reactive cationic intermediate (Figure 3.6a). It is unlikely that DMPX and stannic chloride behave in a similar manner and a more feasible mechanism is proposed on Figure 3.6b. Elemental analysis has shown that the stoichometry of the complex to be 1:1 but if this complex were momomeric in nature, it would be difficult to propose a mechanism whereby (lll) could be produced. The dimeric structure, shown on Figure 3.6b, accounts for the formation of (lll) and is attractive as it incorporates both the lone pairs of the diether, co-ordinated to the central tin nucleus, to give a stable, hexa co-ordinated, sterically favoured structure. In contrast to DCMB, the DMPX intermediate is stable and the reverse reaction to monomer and catalyst is thought to be negligibel. This may be attributed to the greater stability of a tin oxygen bond (BE 133 Kcal), as compared with a tin chloride bond (BE 74 Kcal)[56].

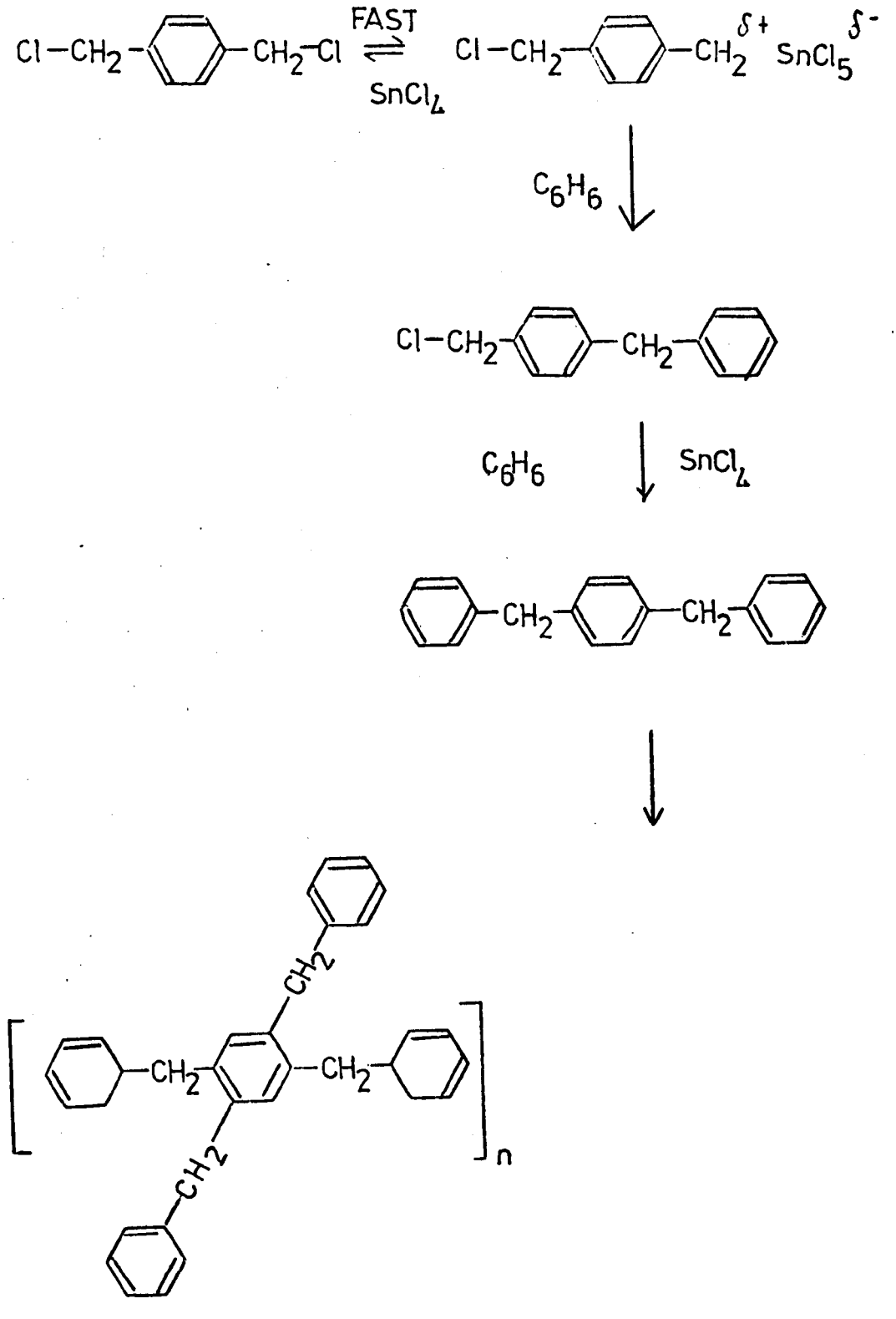
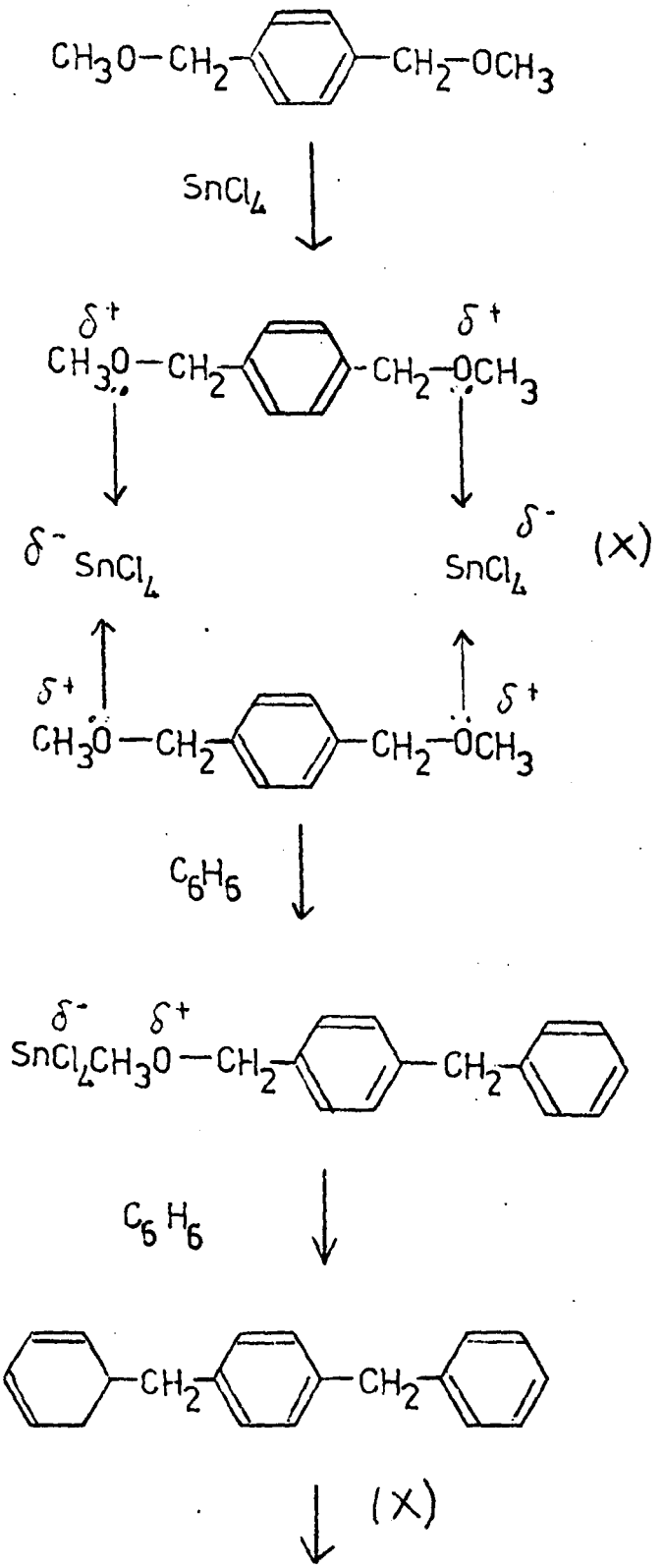


Figure 3.6(a)



POLYMER

Figure 3.6(b)

Again in contrast with the DCMB polymerisation, the condensation product, in this case methanol, is not liberated in DMPX polymerisation but exists as part of complex with stannic chloride so that the stannic chloride is converted first of all to an active 1:1 complex with methanol and subsequently to an inactive 2:1 methanol:stannic chloride complex. For these reasons, the reaction will stop at any early stage unless concentrations of stannic chloride are equal to or greater than the initial concentration of DMPX. DCMB polymerisations result in the evolution of hydrogen chloride which apparently does not destroy the catalytic activity of the stannic chloride. Indeed an acceleration in the rate as reaction proceeds has been noted[16] and this may be due to a co-catalytic effect of hydrogen chloride. This aspect will be discussed more fully in Chapter four.

From the limited information obtained in these preliminary experiments, it was not possible to ascertain, unequivically the exact mechanism of co-polymerisation of DMPX and benzene. However from these initial experiments certain features of this mechanism can be decided. It is clear that polymerisation occurs via two separate catalysts and through two distinct types of intermediates. Initial reaction occurs via the intermediate complex whose structure is thought to be similar to that of (IV). As reaction proceeds, a 1:1 stannic chloride - methanol complex is formed and reaction between this complex and DMPX results in a new intermediate which is soluble in the reaction solvent and is mot probably ionic in nature (structure V). Further reaction produces the 2:1 adduct ($CH_3OH:SnCl_4$) which is inactive as a Friedel Crafts catalyst, owing to the fact that the tin atom is now surrounded by six ligands and further complexing with DMPX would be sterically hindered. A possible mechanism for the first two stages of reaction involving the stannic chloride - methanol complex is given on Figure 3.7.

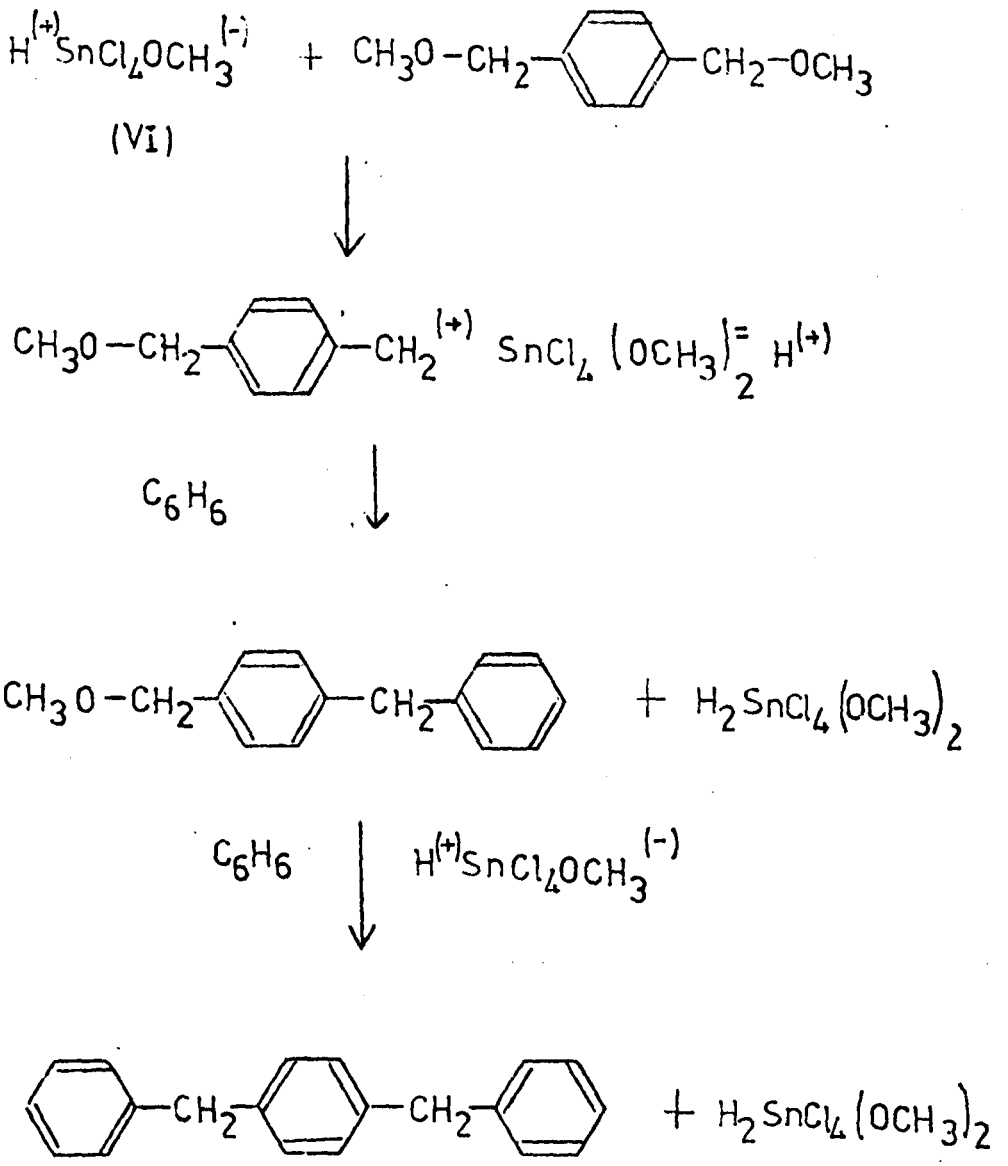

H(+)SnCl4OCH3(-)
(VI)
CH3O-CH2
CH2-OCH3
CH3O-CH2
CH2(+)
SnCl4 (OCH3)2= H(+)
C6H6
CH3O-CH2
CH2
+ H2SnCl4(OCH3)2
C6H6
H(+)SnCl4OCH3(-)
CH2
CH2
+ H2SnCl4(OCH3)2

Figure 3.7

Clearly a large number of parameters affect the kinetics of DMPX polymerisation; for example, the reaction proceeds by two different mechanisms in a heterogeneous and homogeneous media at different stages. Thus kinetic analysis of this system becomes extremely complex and the treatment of the kinetics of the DCMB polymerisations cannot be applied to the DMPX system. Simplification of the system must be made before any meaningful kinetic examination is carried out. Under vacuum, it was impossible to remove methanol by evolution during the course of reaction, and in any case an azeotropic mixture of benzene and methanol is formed. It is possible, however, to eliminate the first stage of the reaction which proceeds via the insoluble intermediate by the introduction of methanol to the starting reaction mixture. Consequently, in kinetic experiments, described in the next chapter, methanol was added in concentrations equal to that of stannic chloride so as to produce a 1:1 methanol-stannic chloride complex and the reaction is assumed to proceed exclusively through this catalyst. The consumption of this catalyst may then be taken account of in the mathematical treatment of the results. A further complicating feature is the effect of the dielectric constant of the solution upon the rate of reaction. A change in benzene concentration changes the solution dielectric constant and it is therefore not possible to accurately estimate the order of reaction with respect to benzene by varying its concentration. Thus in all kinetic experiments, the benzene concentration was kept constant and in high excess relative to DMPX.

In spite of these obvious difficulties, it was still possible to carry out a limited kinetic examination of the DMPX polymerisation in order to shed more light on the mechanism of reaction and to correlate this with the structure of the final polymers and ultimately with their thermal stability. Thus the relative reactivities of the two methoxyl groups of (I) and the single methoxyl group in (II) may be compared, and this information

is particularly useful in discussing the probably structure of the final polymer as in chapter five. Comparison of these kinetic results may be made with the results of previous workers on similar systems and the nature of the polymers compared.

CHAPTER 4

KINETICS OF CO-POLYMERISATION OF DMPX AND BENZENE

4.1 Introduction

In the preceeding chapter, it has been shown that $\alpha\alpha'$ dimethoxy-p-xylene (DMPX) may be co-polymerised with benzene in the presence of stannic chloride. In order to deduce the mechanism of polymerisation and subsequently to account for the structural properties of the polymer, a kinetic analysis of the initial stages of polymerisation was carried out. The approach to these kinetic experiments was governed by the results of preliminary investigations described in Chapter three.

The present chapter gives an account of the kinetics of the first two steps in the co-polymerisation of DMPX and benzene and the results are compared with those of Grassie and Meldrum[16] for a corresponding system using di(chloromethyl) benzene (DCMB) as monomer.

4.2 Quantitative Analysis by GLC

As noted in Chapters three and five DMPX (I) and the first two product of its reaction with benzene, may be separated using GLC. As discussed previously, the reaction may be controlled such that (II) and (III) are virtually the sole products of reaction at a specified time. Since GLC is an effective method of estimating the concentrations of each of these components at regular intervals, a kinetic analysis of the first two stages of polymerisations may be carried out. Using a 1% silicone gum column (1% SE/30), an efficient separation of (I), (II) and (III) and toluene, which was used as an internal standard, was achieved (Table 4.1, Figure 4.1).

TABLE 4.1

Retention (Time) (Min.)	Conditions	Component
5	Isothermal 25°C	Toluene
20	Prog. from 50°- 5°/min. to 125°C	(I)
28	Prog. 5°/min. to 175°C	(II)
36	Prog. 5°/min. to 215°C	(III)

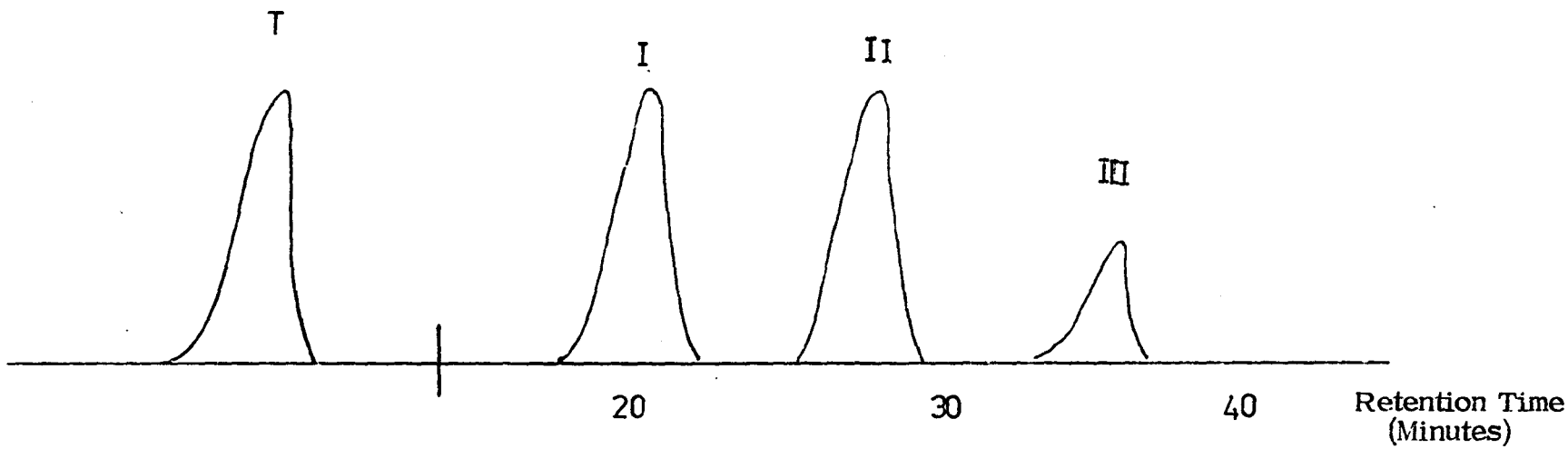


Figure 2.1

Calibrations were carried out to determine the flame sensitivity of (1), (11) and (111) relative to toluene. Mixtures of (1), (11) and (111) and toluene of varying compositions were injected and from the resulting G.L.C. traces, the areas under each peak were estimated by weighing Xerox cut outs. A sensitivity factor for each component relative to toluene was then obtained by measuring the slope of the linear plot of peak areas against composition ratios by weight which follows equation 4.1:-

$$\frac{\text{Weight of (1), (11) or (111)}}{\text{Weight of toluene}} = K \frac{\text{Area under peak (1), (11) or (111)}}{\text{Area under toluene peak}}$$

From the slopes of the three linear plots, (Tables 4.2a, b, c Figures 4.2a, b, c) values of K were obtained as follows:

$$K_{(1)} = 2.40$$
$$K_{(11)} = 1.43$$
$$K_{(111)} = 2.63$$

The concentration of (1), for example, may be estimated at any time if 0.5g of toluene is added to a 5 ml aliquot of reaction solution, by the following calculation:-

$$\frac{W_{(1)}}{W_T} = K_{(1)} \frac{A_{(1)}}{A_T}$$

$$W_{(1)} = 2.40 \times \frac{A_{(1)}}{A_T} \times 0.5$$

$$W_{(1)} = \frac{2.40 \times 0.5}{166} \times \frac{A_{(1)}}{A_T}$$

$$(1) = \frac{200 \times 2.40 \times 0.5}{166} \frac{A_{(1)}}{A_T}$$

$$(1) = 1.45 \frac{A_{(1)}}{A_T} \text{ moles/litre}$$

TABLE 4.2(a)

$W_{(1)}$ / WT	$A_{(1)}$ / AT
0.46	0.180
0.37	0.156
0.27	0.119
0.18	0.076
0.08	0.042

TABLE 4.2(b)

$W_{(11)}$ / WT	$A_{(11)}$ / AT
0.11	0.061
0.088	0.053
0.073	0.044
0.016	0.012
0.008	0.004

TABLE 4.2(c)

$W_{(111)}$ / WT	$A_{(111)}$ / AT
0.088	0.033
0.053	0.024
0.044	0.017
0.022	0.009
0.015	0.007

Figure 4.2(a)

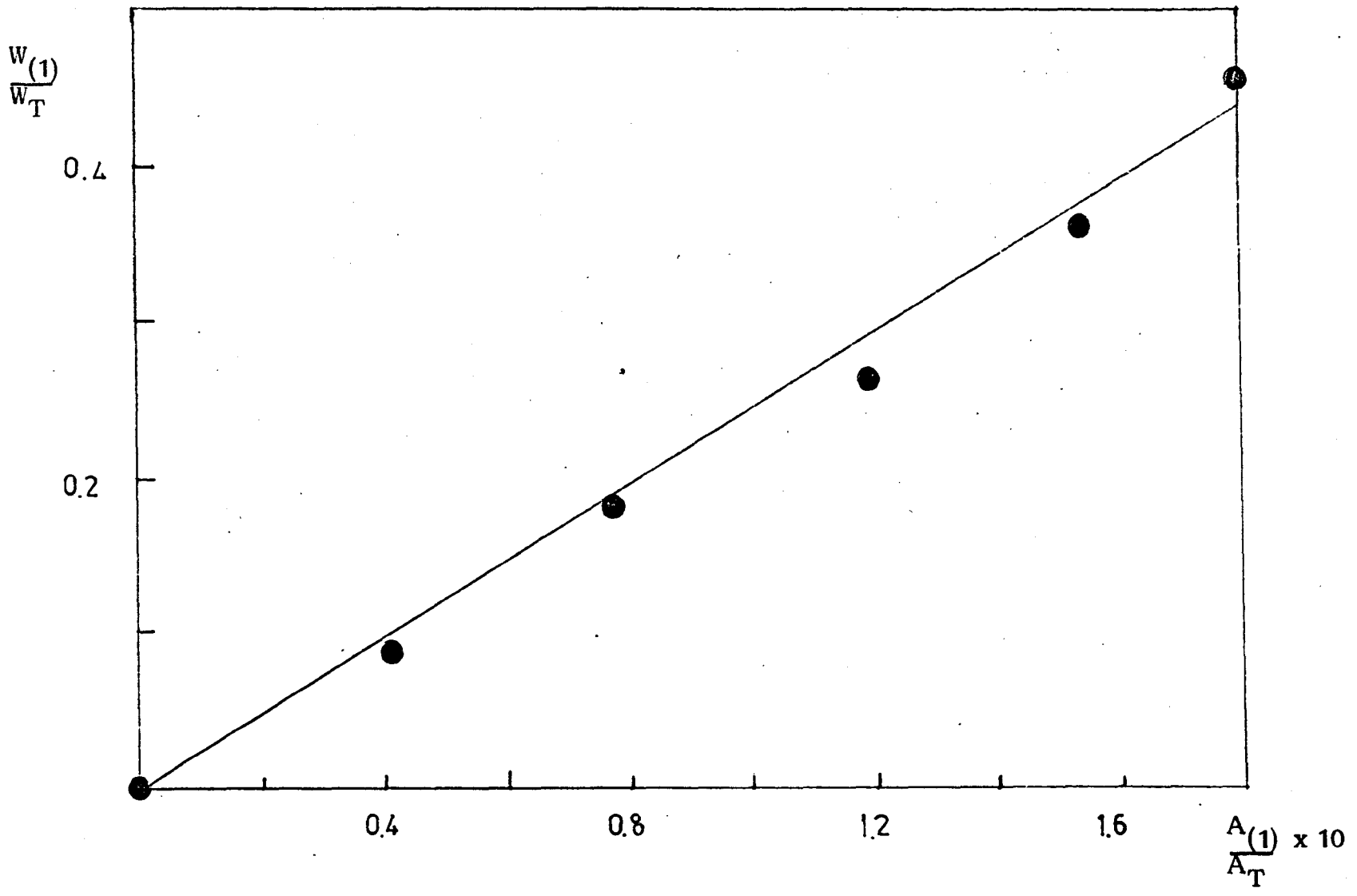
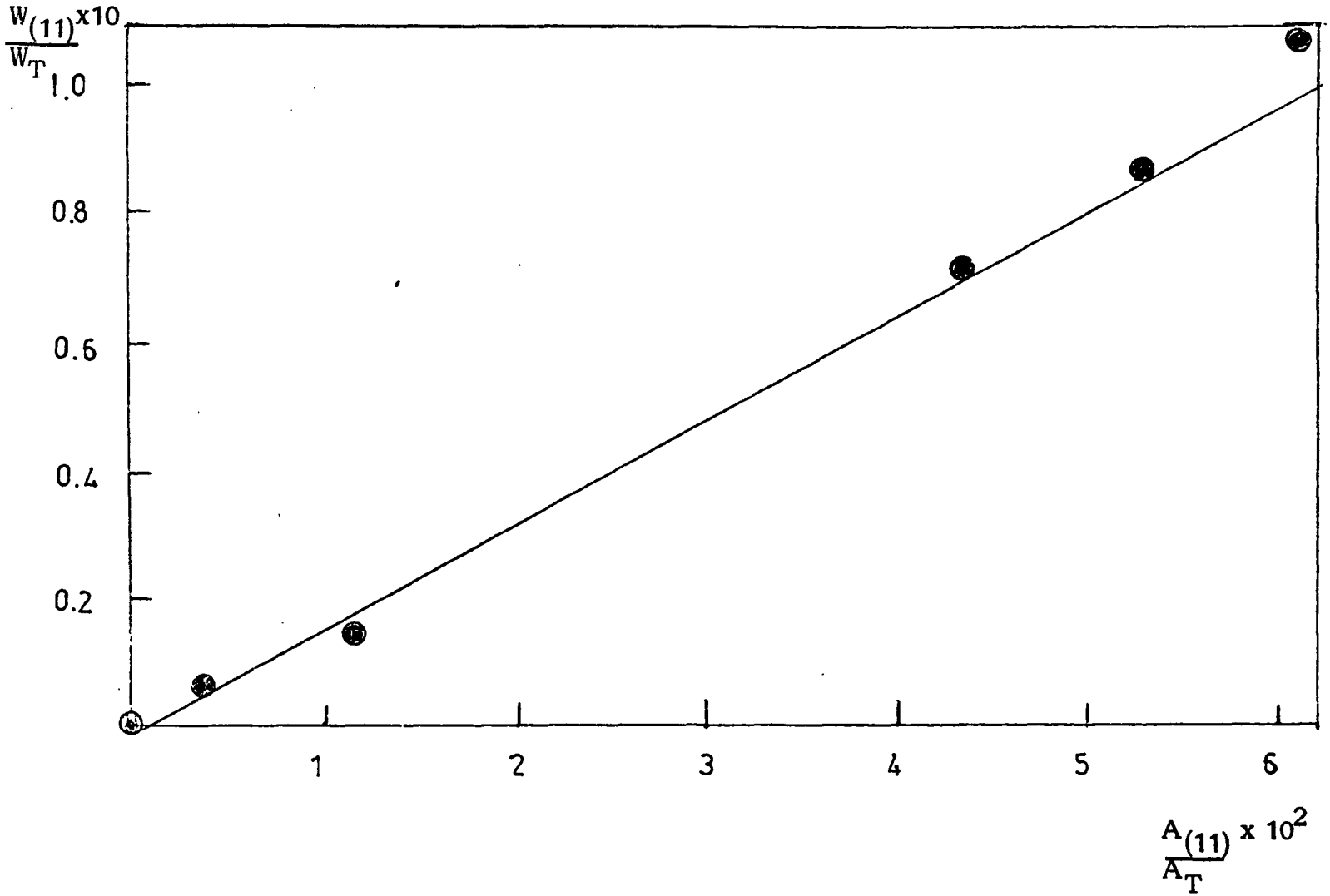


Figure 4.2(b)



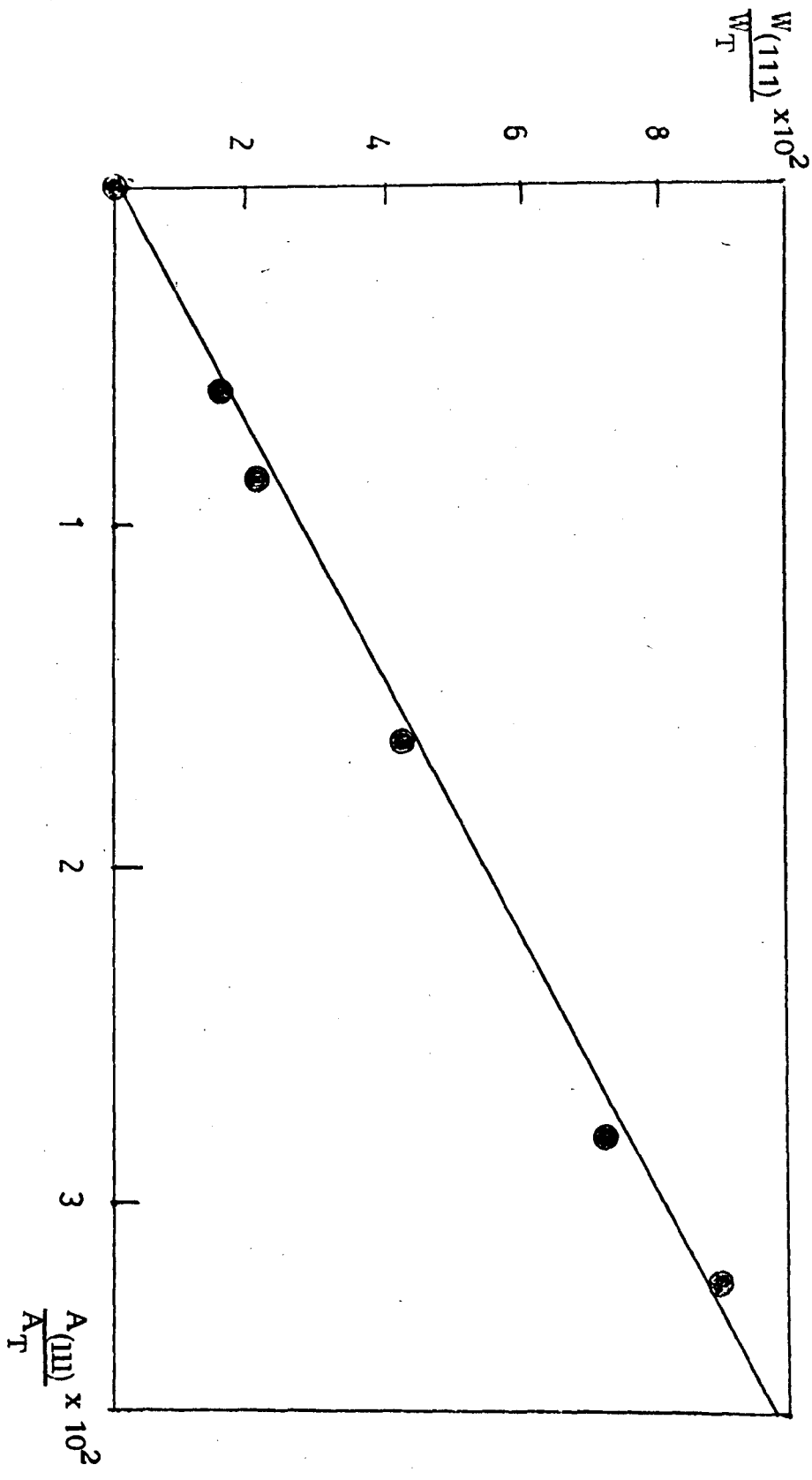
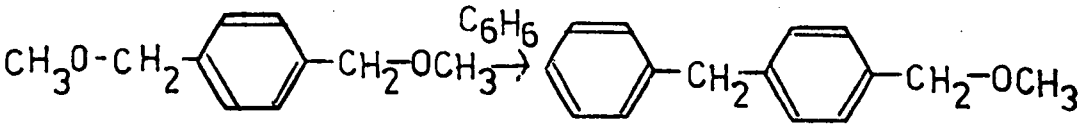


Figure 4.2(c)

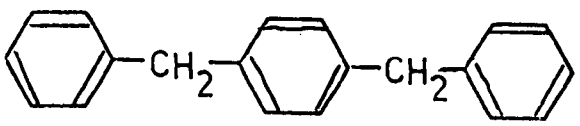
The concentrations of (II) and (III) may be calculated in a similar manner.

4.3 Kinetics of Polymerisation

As noted in chapter three, the first two stages of co-polymerisation of DMPX (1) and benzene result in the production of (II) and (III)



(I) (II)



(III)

The aim of this investigation was to obtain values for the composite rate constants of the two reactions shown above.

As established in chapter three, the polymerisation proceeds by the initial formation of a co-ordinated stannic chloride - DMPX complex which rearranges to produce a stannic chloride-methanol adduct which is the active catalyst in the later stages. In chapter three, it is also noted that the reaction medium is heterogeneous while the stannic chloride - DMPX complex is present but becomes homogeneous when re-arrangement to the stannic chloride-methanol complex is complete. For this reason the kinetic examination was restricted to the polymerisations catalysed by the soluble stannic chloride-methanol complex. This was possible by first preparing the stannic chloride-methanol adduct by using equimolar amounts of methanol and stannic chloride in the initial mixture as described in

Chapter two.

1, 2 dichloroethane and nitromethane were both used as solvents in this investigation. In order to compare these results with those of Grassie and Meldrum[16], who used DCMB as monomer and dichloroethane as solvent, it was thought desirable to use dichloroethane as solvent. For reasons, discussed later, the larger part of this investigation was carried out using nitromethane, in which the catalytic complex is highly soluble. It was also thought that a comparison of the rates of reaction in solvents of various polarities might assist in deducing the reaction mechanism. All kinetic experiments were carried out in the absence of water using the system described in chapter two.

For the reasons outlined in chapter three, it was not possible to estimate reaction order with respect to benzene. Its concentration is therefore maintained in high excess of DMPX, thoughout and is taken as constant. However, by varying initial concentrations of DMPX and catalyst and measuring the initial rate of disappearance of DMPX it was possible to find the order of the first reaction with respect to each of the two components. Figures 4.3 a, b, c, 4.4 a, b and 4.5 a, b illustrate the change in concentration of (I), (II) and (III) as a function of time using three separate initial concentrations of (I) and maintaining the initial concentration of catalyst and benzene constant, in nitromethane. Figure 4.6 (Table 4.6) is a plot of initial rate of disappearance of (I) against initial concentration of (I). From this it is clear that the reaction is not first order with respect to DMPX and it is apparent that the initial rate of disappearance of (I) is independant of the initial concentration of (I).

TABLE 4.3

(I) moles/litre x 10	(II) moles/litre x 10^2	(III) moles/litre x 10^3	Time minutes
1.20			0
1.15	0.40	0.10	15
1.12	0.80	0.20	30
1.09	0.82	0.41	60
1.09	0.11	0.78	120
1.06	0.12	1.05	180
1.07	0.11	1.50	300

$(Catalyst)_o$ = 0.044 M

$(Benzene)_o$ = 1.13 M

in CH_3NO_2 solvent

TABLE 4.4

(I) moles/litre x 10^2	(II) moles/litre x 10^2	(III) moles/litre x 10^2	Time minutes
6.00			0
5.51	0.50	0.10	15
5.22	0.60	0.20	30
4.74	0.89	0.36	120
4.63	1.01	0.38	180
4.31	1.03	0.54	330
4.10	1.16	0.83	480

$(SnCl_4)_o$ = 0.044 M $(C_6H_6)_o$ = 1.13 M

solvent CH_3NO_2

TABLE 4.5

(I) moles/litre x 10^2	(II) moles/litre x 10^3	(III) moles/litre x 10^3	Time minutes
2.40			
1.80	4.01	2.02	15
1.61	4.02	4.04	30
1.33	6.04	5.05	45
1.11	7.01	6.02	60

$(SnCl_4)_o$ = 0.044 M $(C_6H_6)_o$ = 1.13 M CH_3NO_2 solvent

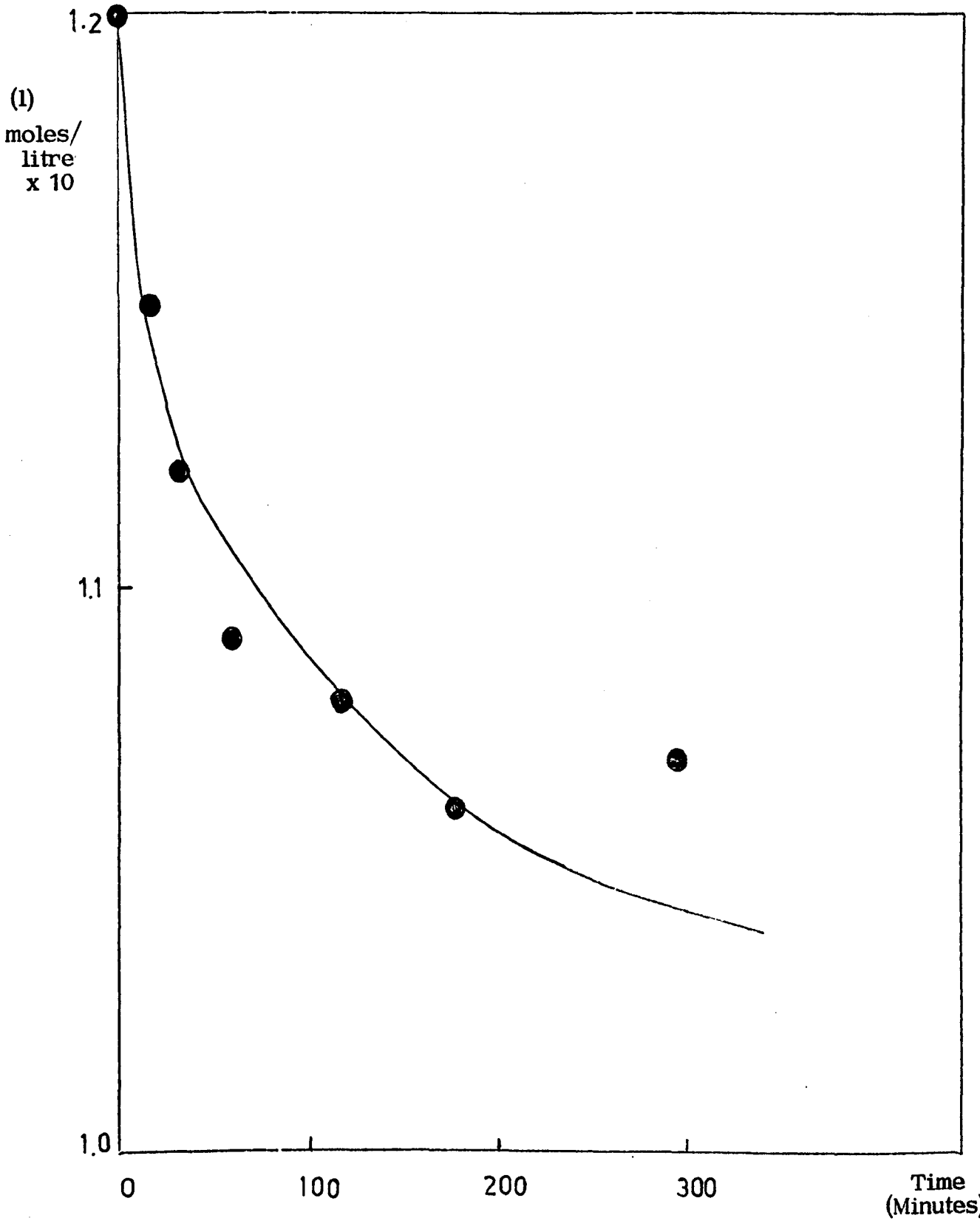


Figure 4.3(a)

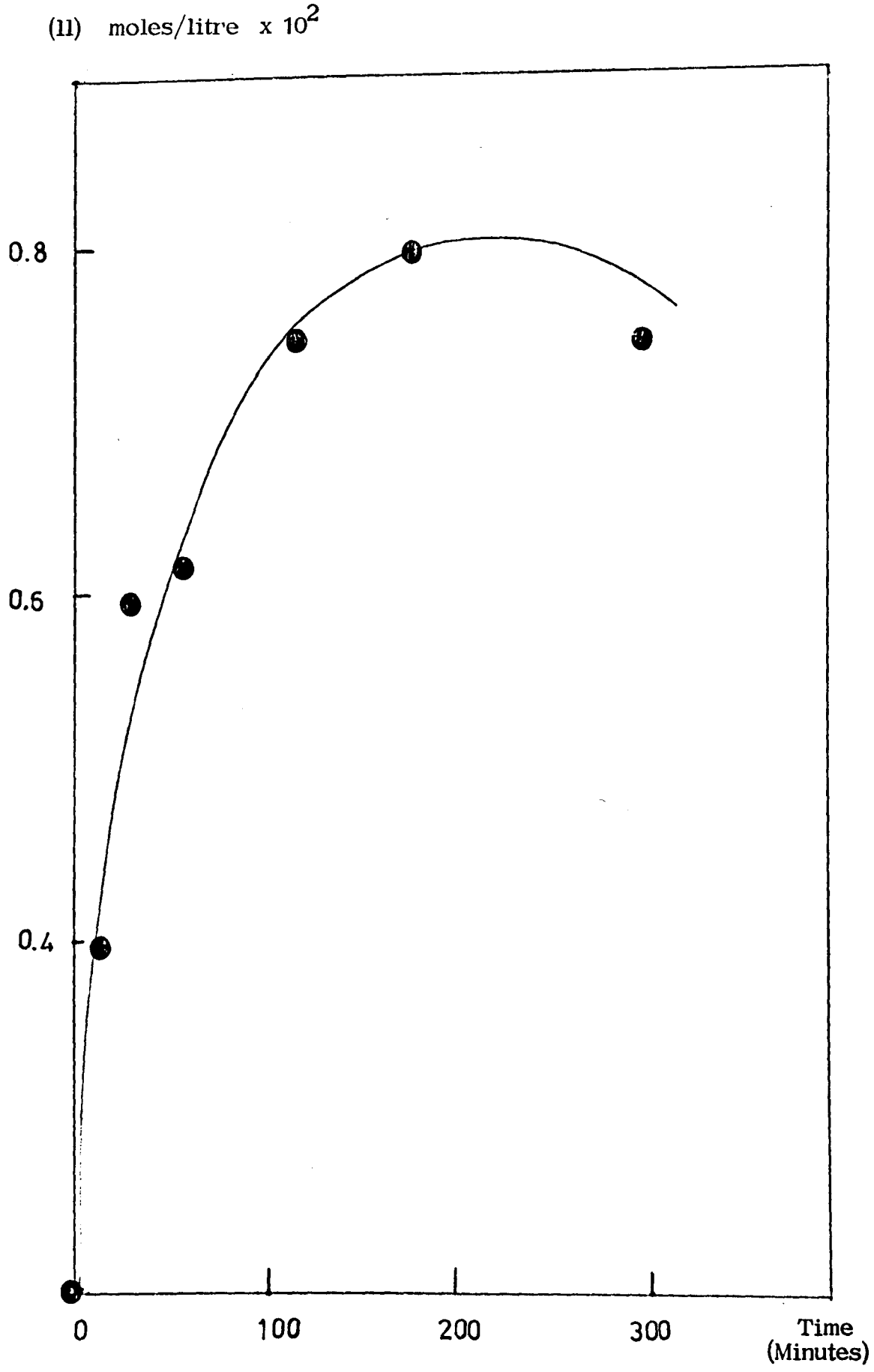


Figure 4.3(b)

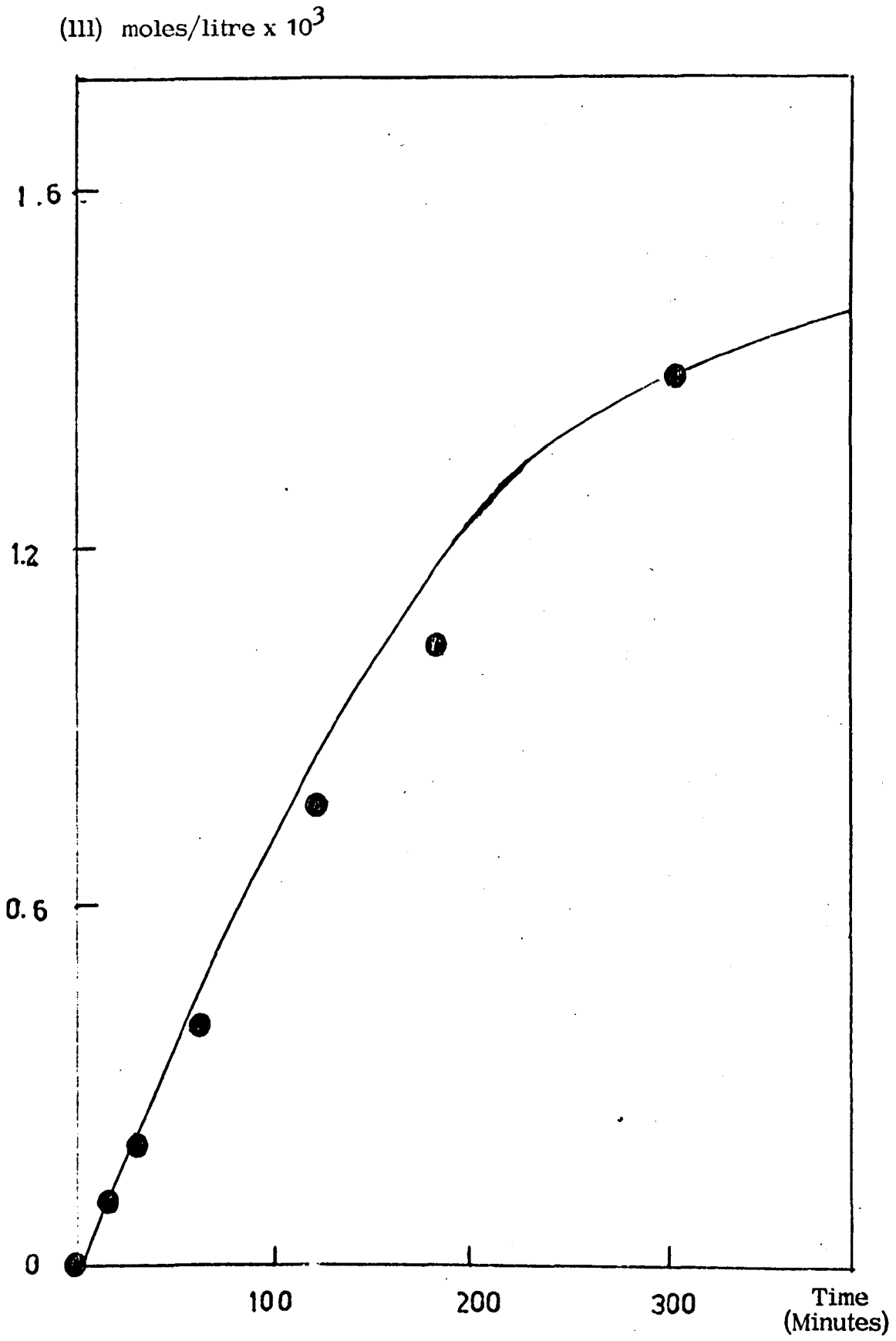


Figure 4.3(c)

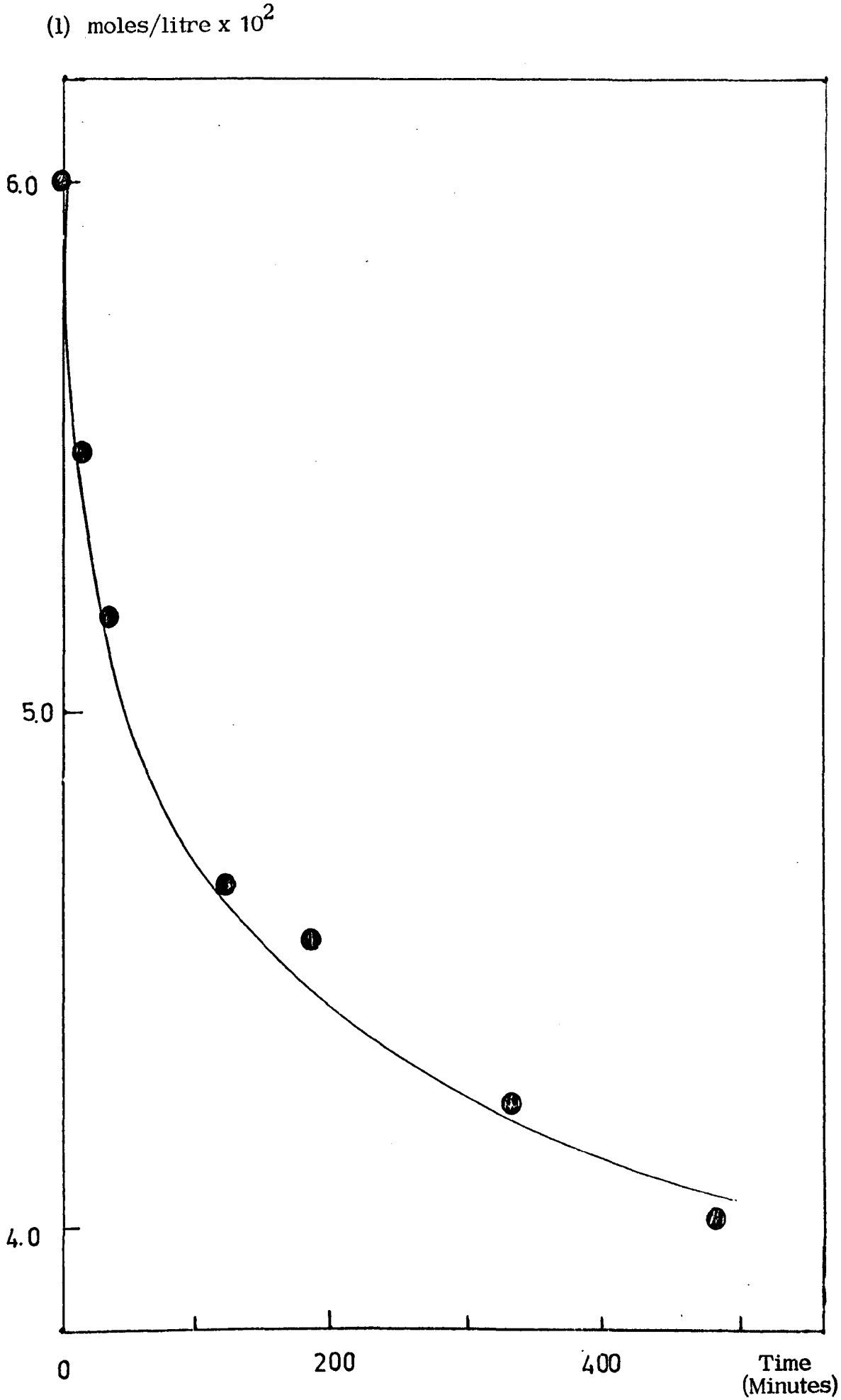


Figure 4.4(a)

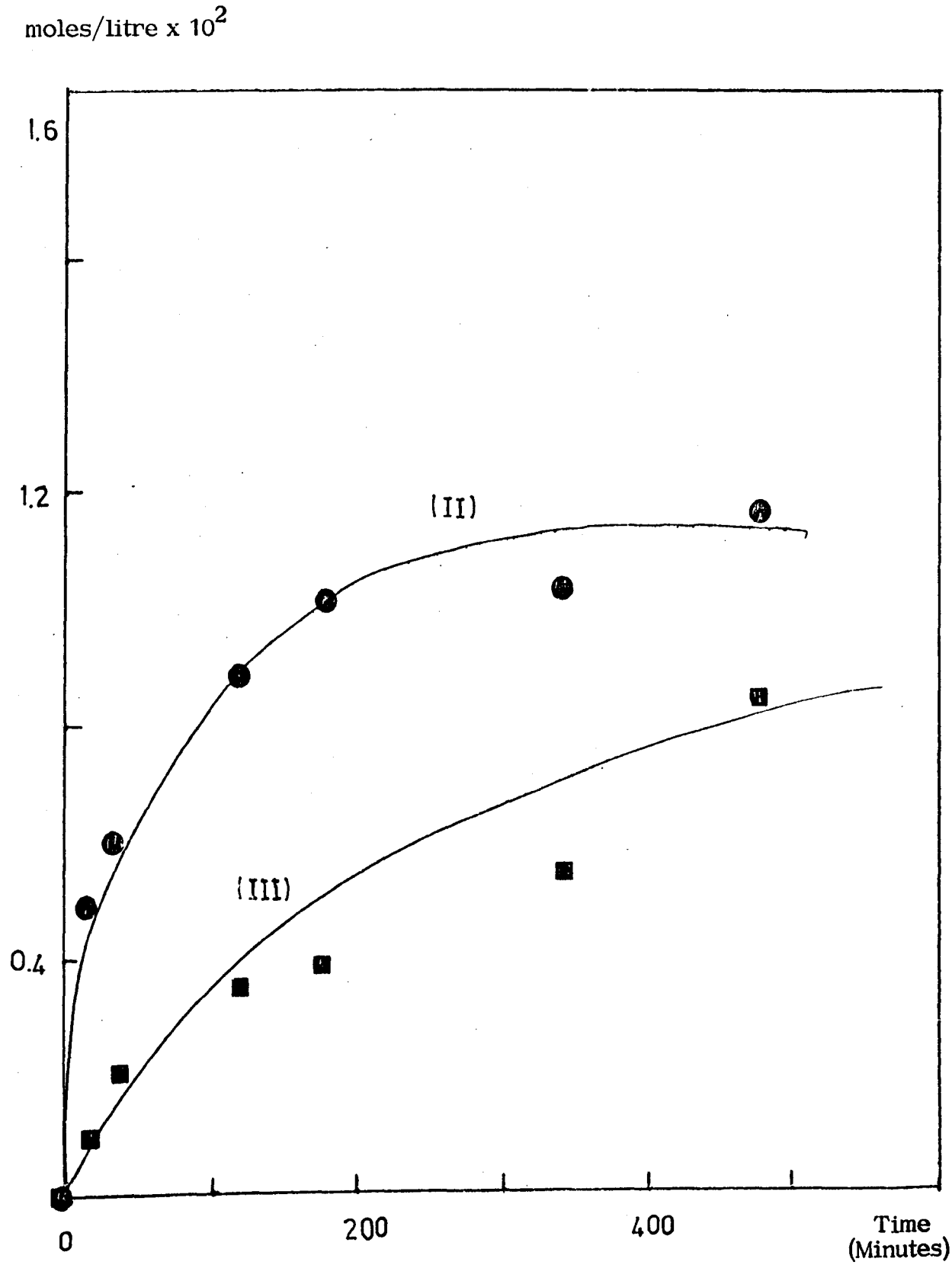


Figure 4.4(b)

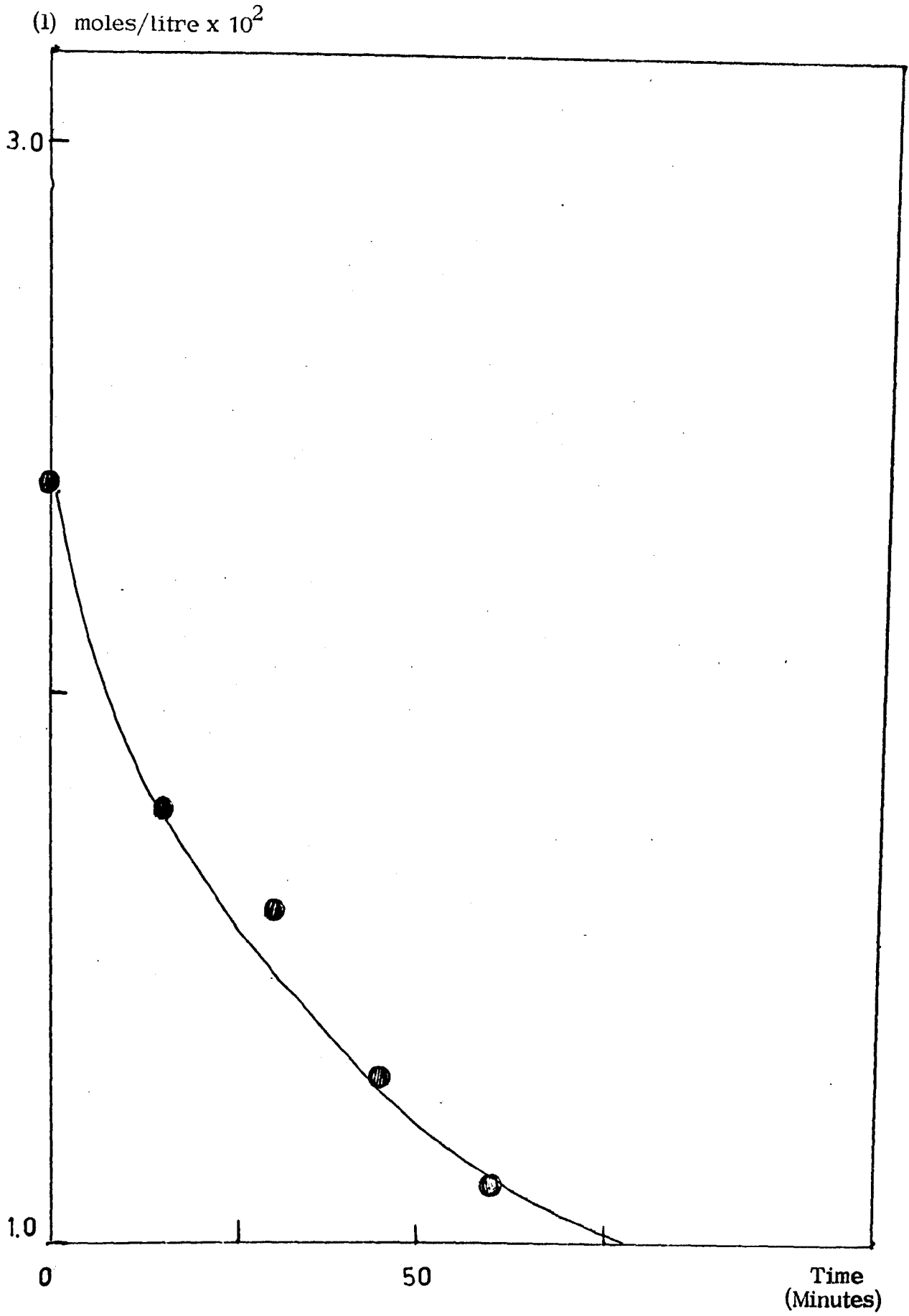


Figure 4.5 (a)

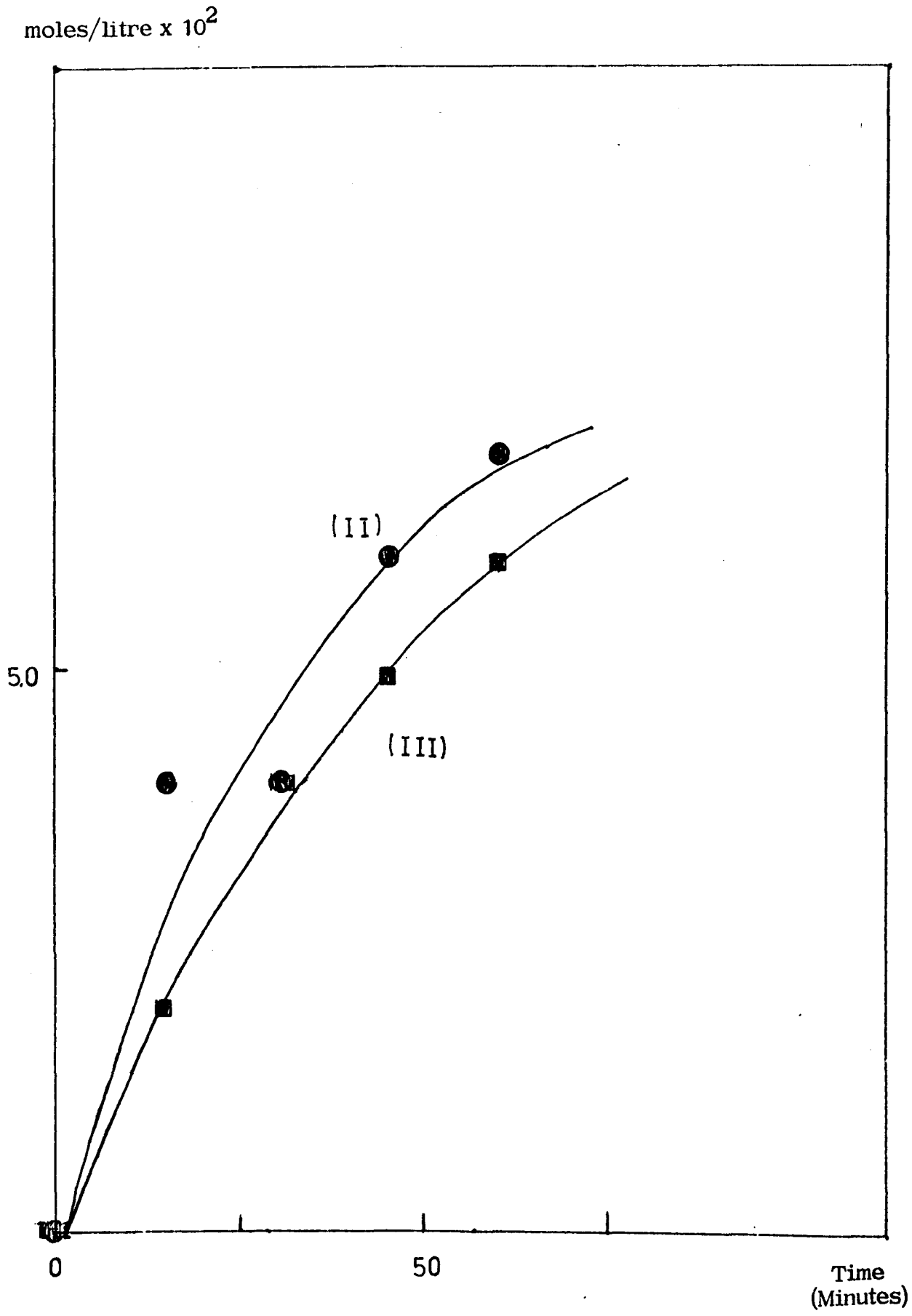


Figure 4.5 (b)

TABLE 4.6

Initial Rate of Disappearance of (1) moles/litre/sec	Initial Concentration of (1) moles/litre x 10
5.6×10^{-6}	1.20
5.6×10^{-6}	0.60
6.7×10^{-6}	0.24

$(SnCl_4)_o = 0.044$ M

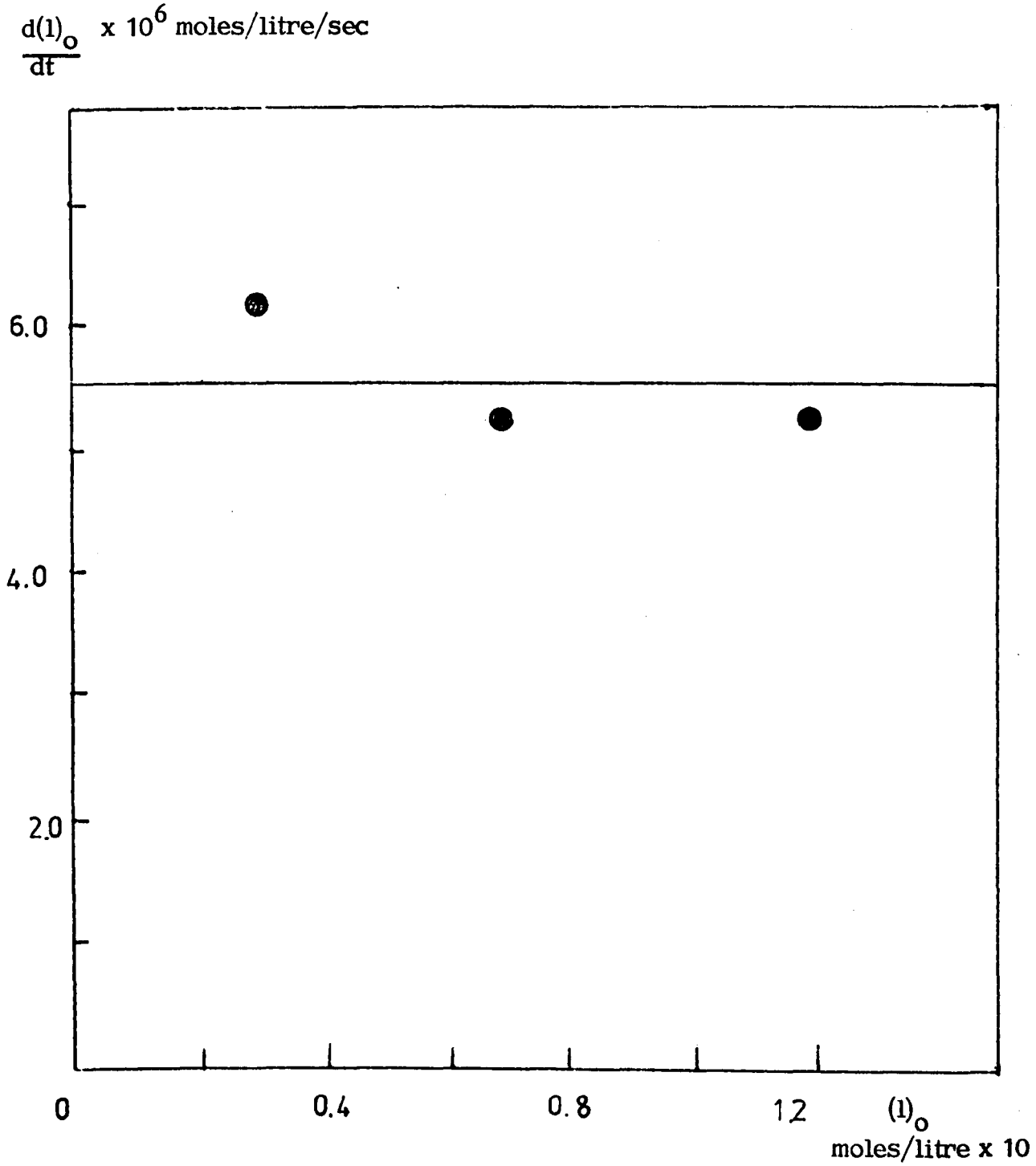

$\frac{d(1)_o}{dt}$ x 10^6 moles/litre/sec
6.0
4.0
2.0
0
0.4
0.8
1.2
$(1)_o$
moles/litre x 10

Figure 4.6

In order to establish the order of the first reaction with respect to catalyst, initial rates of reaction were measured, whilst varying the initial concentration of catalyst and maintaining $(l)_o$ constant. The results of these investigations are illustrated in Figures 4.4a, b, 4.7 a, b 4.8 a, b (Tables 4.4., 4.7, 4.8)

Here the loss of (l) and production of (ll) and (lll) are plotted against time using three separate initial concentrations of catalyst (0.020, 0.044, 0.088 M). Figure 4.9 (Table 4.9) is a plot of the initial rate of disappearance of (l) $\left[\frac{(d(l))}{dt}\right]$ against the initial concentration of catalyst $(C)_o$. Deviation from first order kinetics is illustrated by the curved plot shown in Figure 4.9 while 4.10 illustrates a log plot of $\frac{(d(l))}{dt_o}$ against $(C)_o$.

In the rate equation,

$$\frac{d(l)_o}{dt} = K (l)_o{}^{o} (C)_o{}^{n} (B)_o{}^{m} \qquad 4.2$$

$(l_o)^o = 1$ and $(B)_o{}^m$ is constant

$$\text{Thus} - \log \frac{d(l)_o}{dt} = \log \text{constant} + n \log (C)_o \qquad 4.3$$

This represents the linear plot in Figure 4.10 the slope being n, the reaction order with respect to catalyst (C). A value of $n = 1.96$ may be deduced from Figure 4.10, indicating second order kinetics with respect to the catalyst.

TABLE 4.7

(I) moles/litre x 10^2	(II) moles/litre x 10^2	(III) moles/litre x 10^2	Time minutes
6.00			0
4.49	0.90	0.61	15
3.30	1.03	1.67	30
2.81	0.90	2.11	60
2.42	1.10	2.93	180
1.71	0.90	3.40	300

Initial Concentration of Catalyst = 0.088 M

(C_6H_6) = 1.13 M in CH_3NO_2 solvent

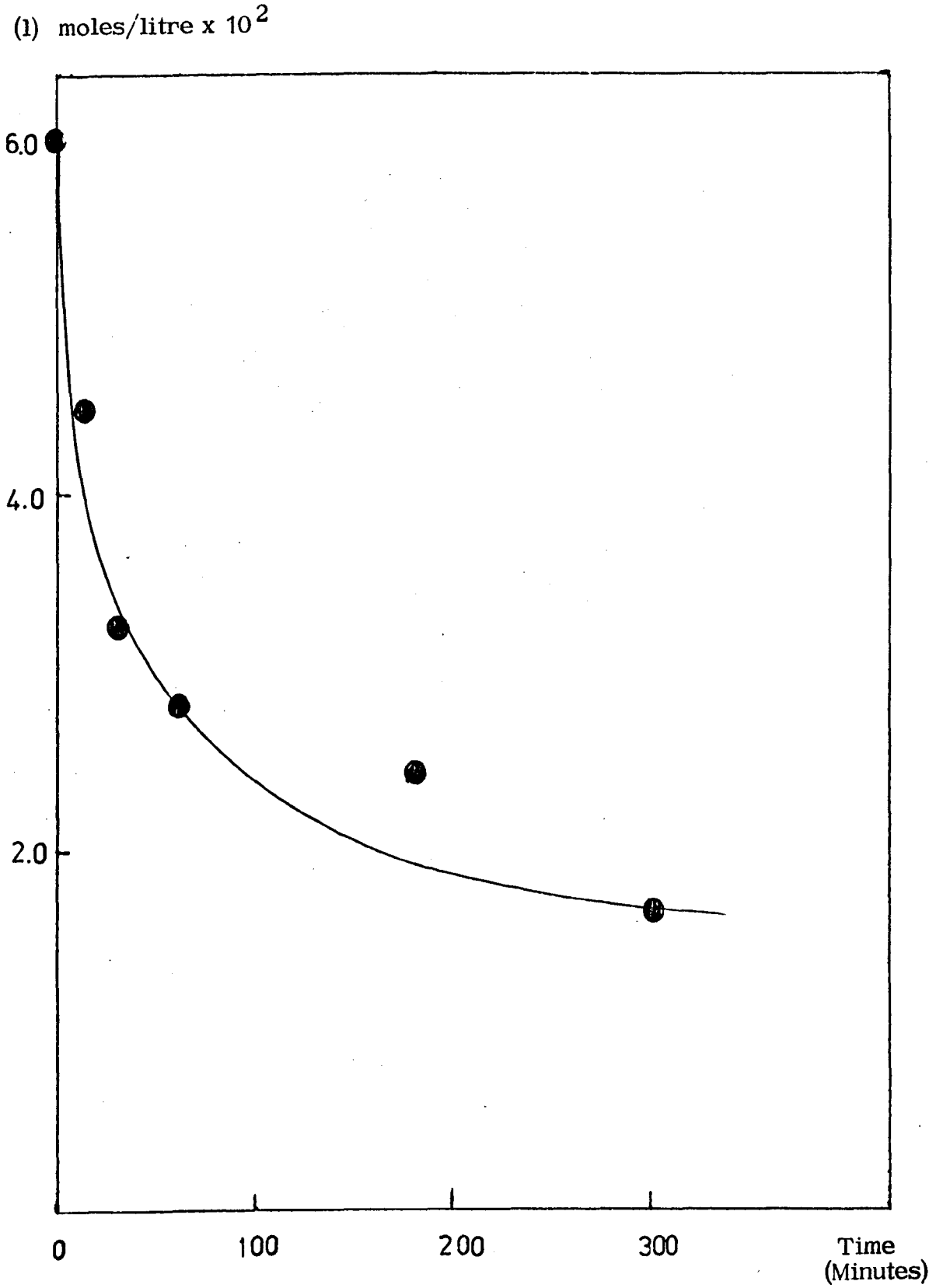


Figure 4.7(a)

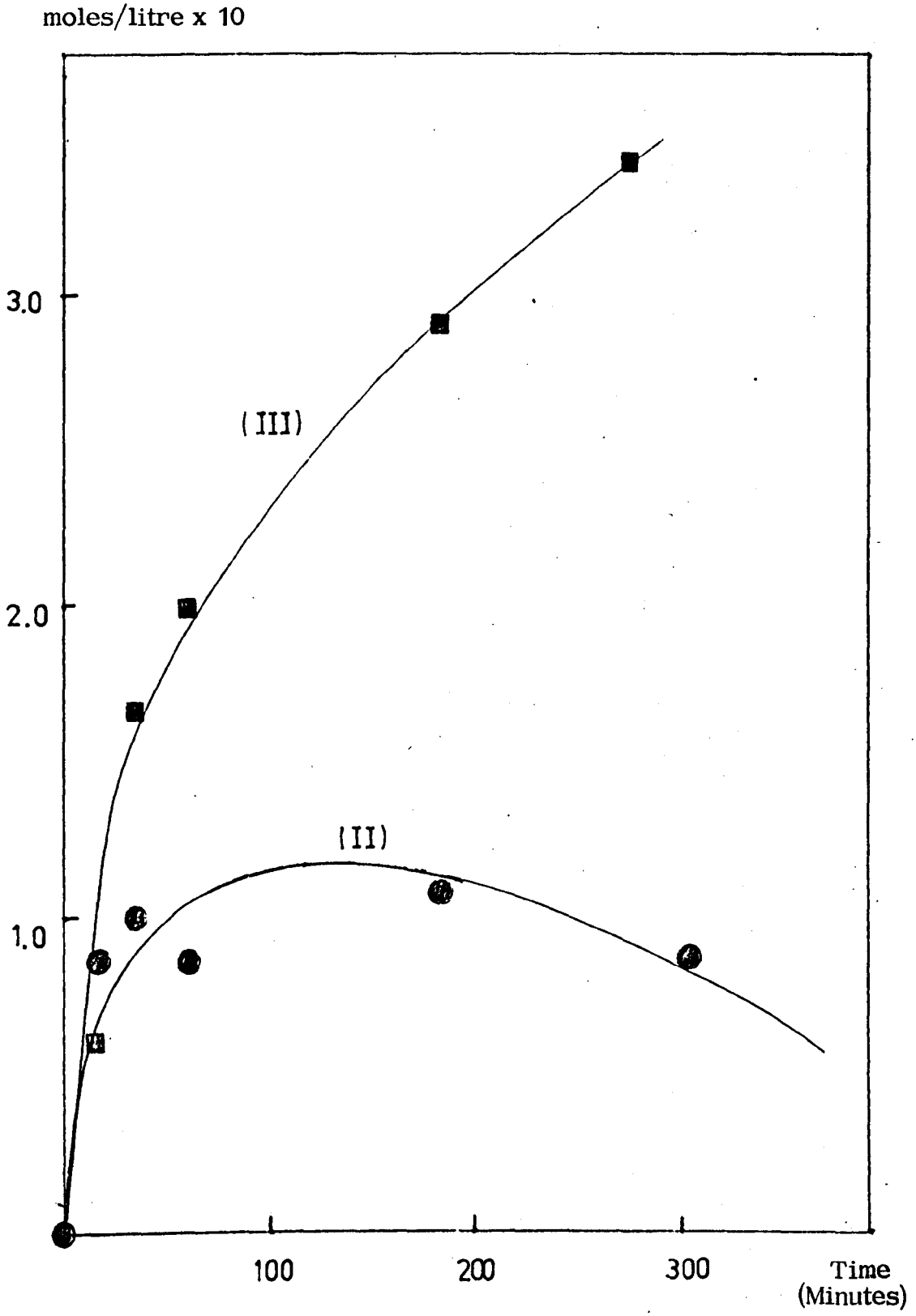


Figure 4.7(b)

TABLE 4.8

(I) moles/litre x 10^2	(II) moles/litre x 10^3	(III) moles/litre x 10^3	Time minute
6.00	0	0	0
5.90	1.0	0	15
5.81	2.9	0	30
5.72	3.1	0	60
5.33	6.1	1.1	120
5.20	9.0	0.9	180
5.20	9.0	0.9	240
5.10	9.1	1.6	360

Initial Concentration of catalyst = 0.020

$(C_6H_6)_o$ = 1.13 M CH_3NO_2 solvent

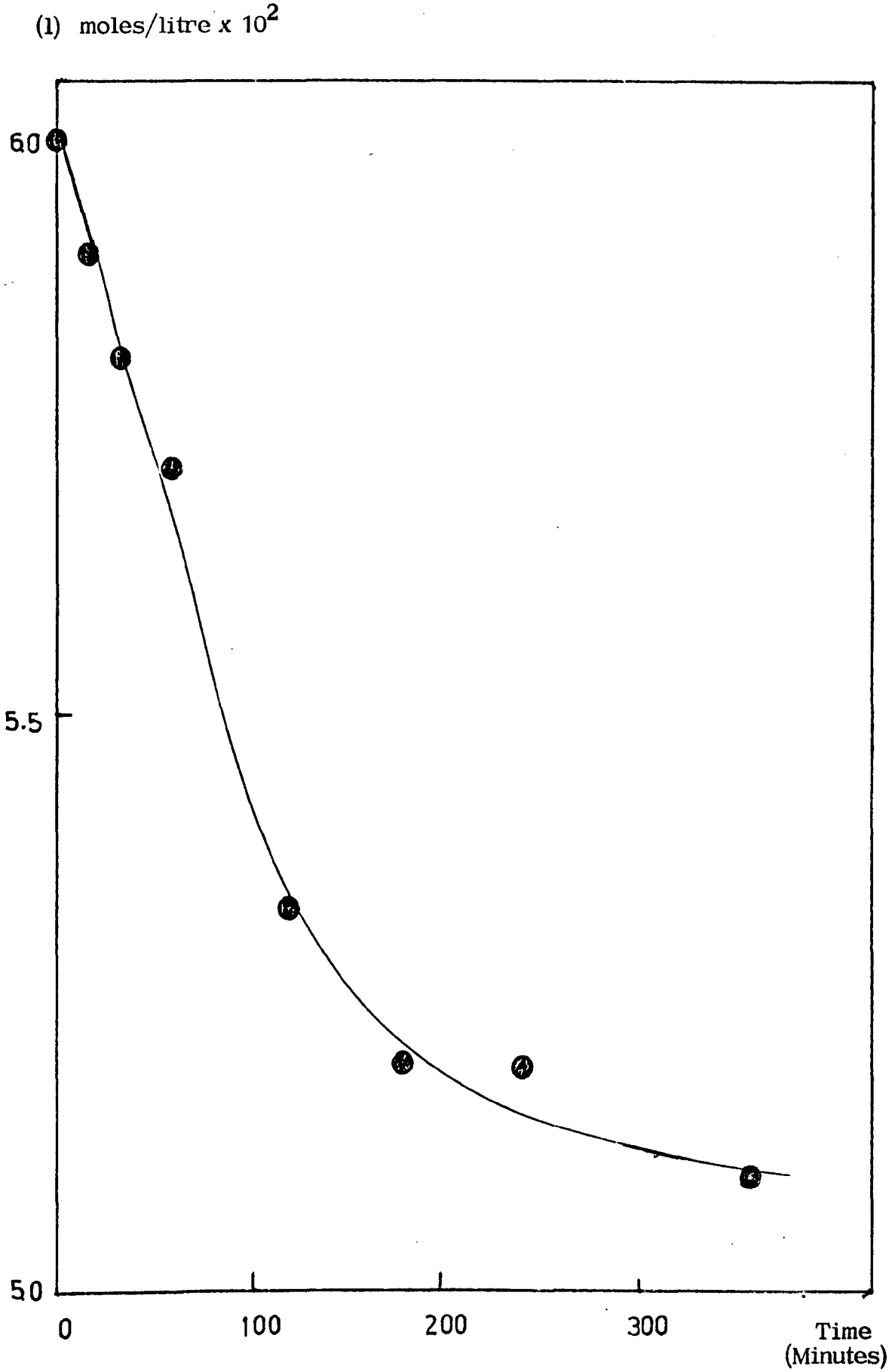


Figure 4.8(a)

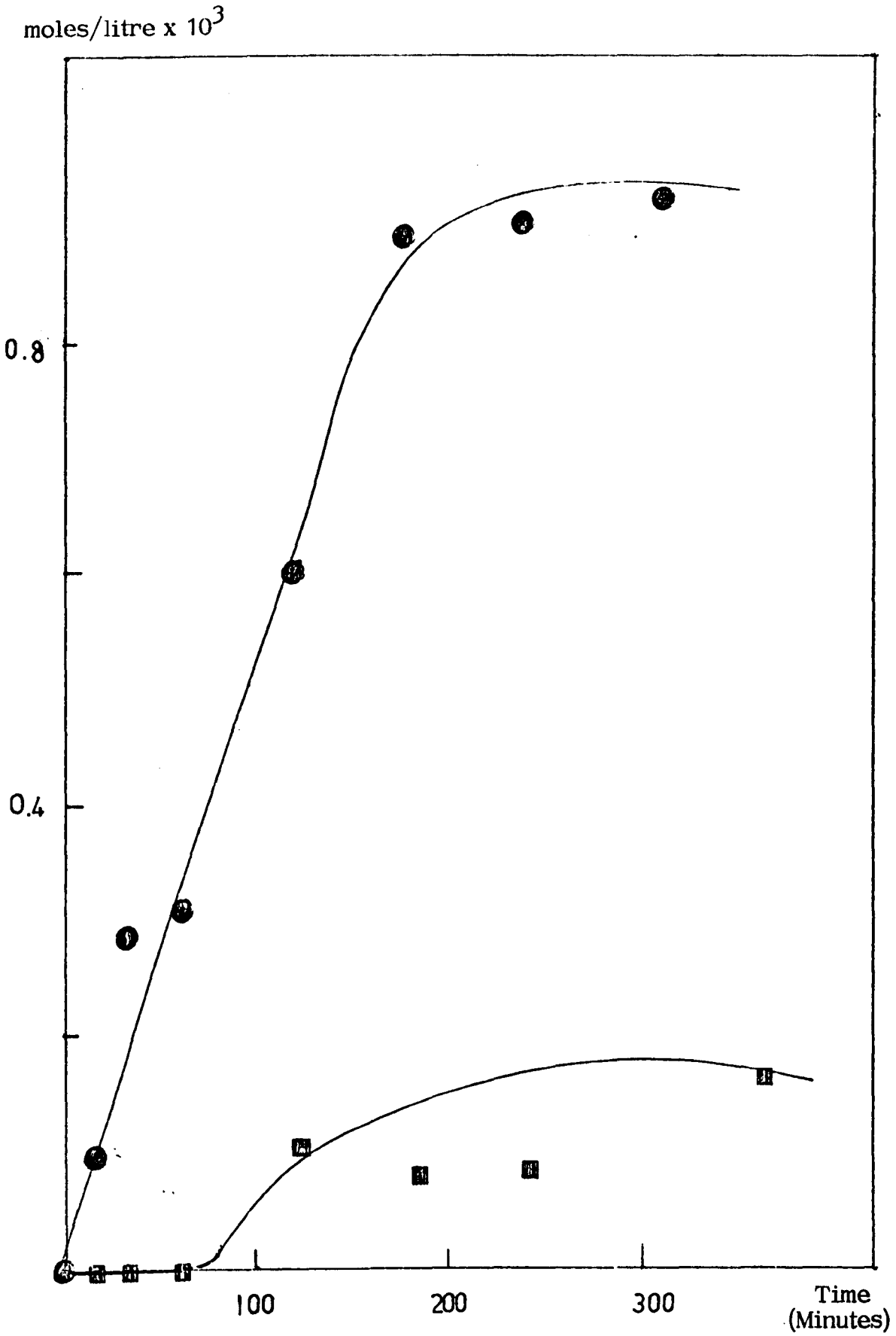


Figure 4.8(b)

TABLE 4.9

$\frac{(-d(I)_o)}{dt}$ moles/litre/sec x 10^5	$(C)_o$ moles/litre x 10^2	$(I)_o$ moles/litre x 10^2
1.72	8.8	6.0 and 12.0
0.56	4.4	6.0
1.33	7.0	9.0
0.12	2.0	6.0

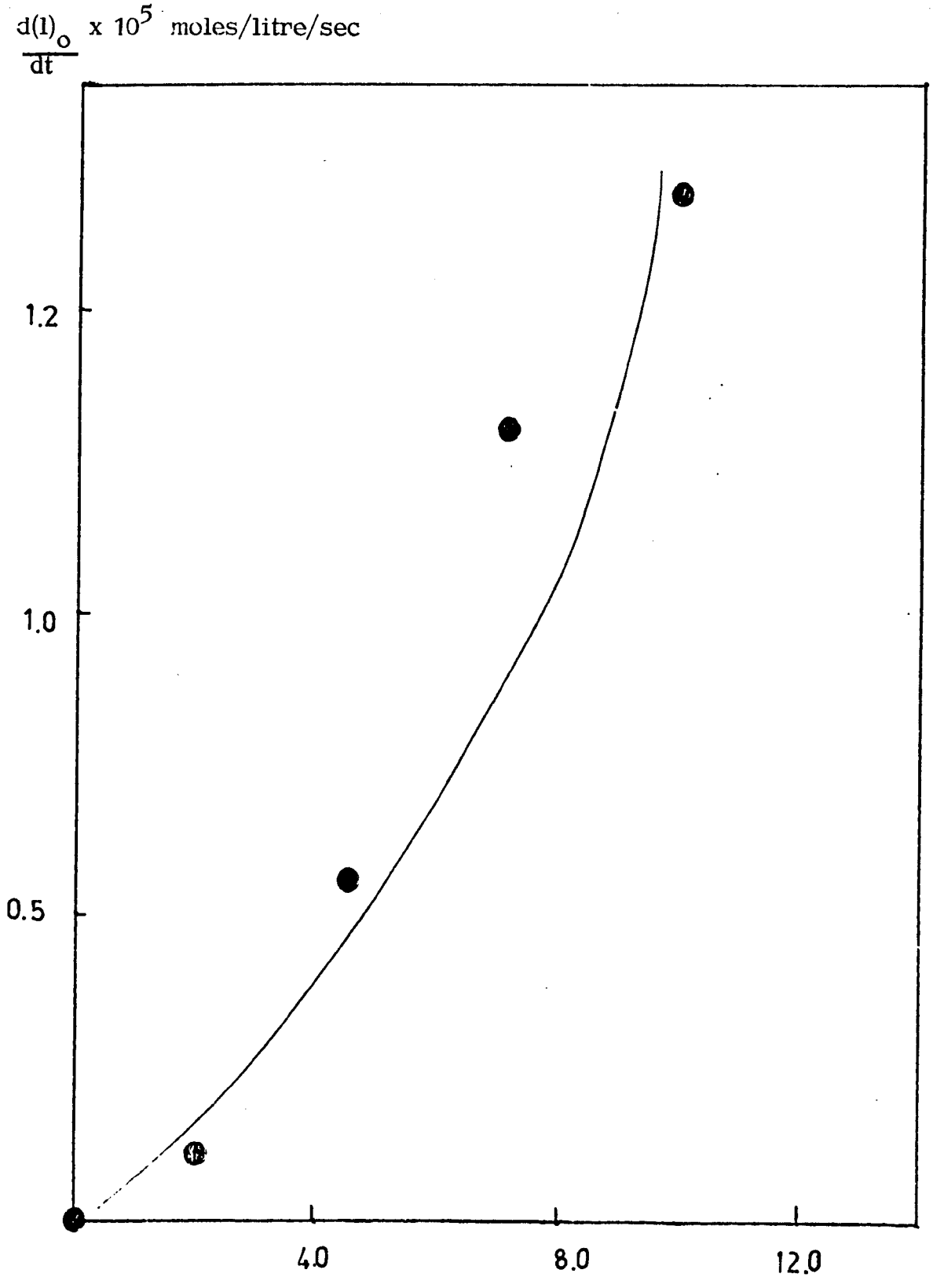

$\frac{d(l)_o}{dt}$ x 10^5 moles/litre/sec
1.2
1.0
0.5
4.0
8.0
12.0
$(l)_o$
moles/litre x 10^2

Figure 4.9

TABLE 4.10

$\log \frac{d_{(l)o}}{dt}$	$-\log (C)_o$
4.73	1.06
4.87	1.15
5.25	1.36
5.92	1.70

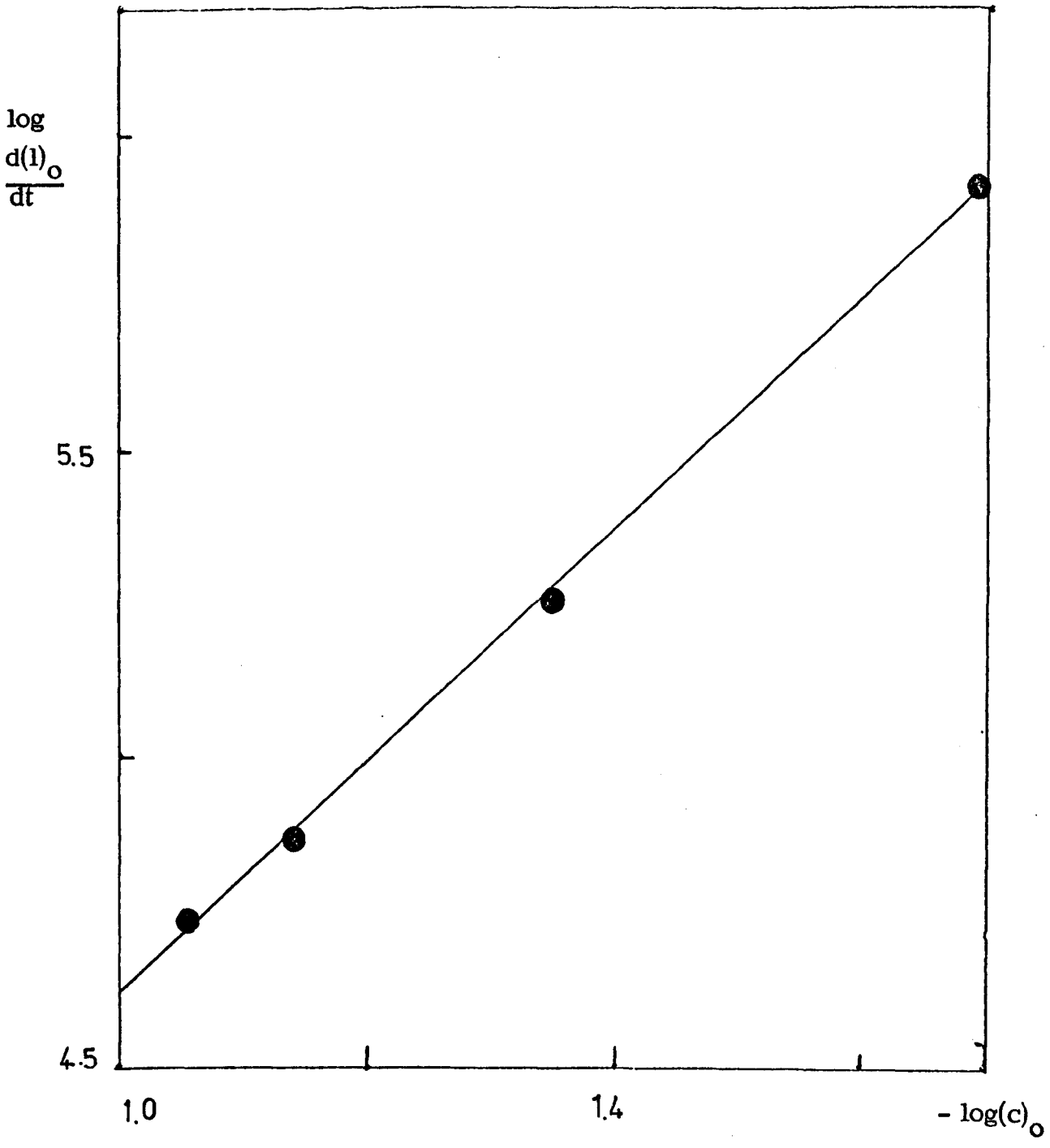


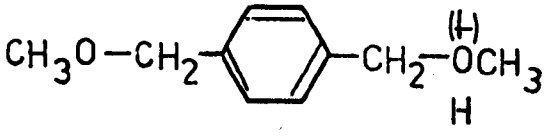
Figure 4.10

Zero order kinetics with respect to monomer and second order kinetics with respect to catalyst indicated that the overall kinetics of the first reaction are complex. A possible explanation for these two unexpected features suggests itself when the structure of the catalyst shown below, as postulated in chapter three is considered.

$$H^{(+)}\ SnCl_4\ OCH_3^{(-)}$$

If the catalyst is ionic in nature, then ion separation may occur in a solution of high dielectric constant.

With this in mind it seems likely that the first stage of the mechanism involves rapid protonation of an oxygen lone pair of the monomer to produce a complex (A)



(A)

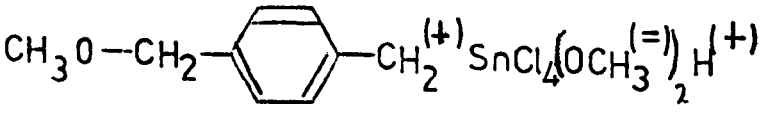
If the equilibrium in this reaction lies largely to the right, then the concentration of (A) will be equal to that of $H^{(+)}$ ions, if the monomer is in excess. Assuming ionisation is complete then the following holds:-

$$(A)_o = (C)_o$$

Following the formation of (A), it is now proposed that a highly polar intermediate (D) is formed by reaction of (A) with ($SnCl_4\ OCH_3^{(-)}$)

(A) + $SnCl_4OCH_3$ -

k-i ⇅ ki FAST



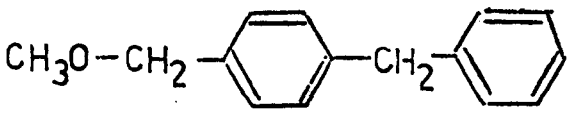
(D)

(D) is a reactive intermediate whose concentration is low at any stage and this allows the stationary state approximation to be applied.

It is proposed that slow reaction of (D) with benzene is the rate determining step. This is supported by the fact that no induction period for the production of (II) is noted in any of the kinetic experiments. An induction period would undoubtedly result if either of the first two stages were slow

(D)

k_{ii} ↓ Slow



(II)

The observed kinetics may now be explained using the stationary state approximation:-

$$\frac{d\,(D)}{dt} = 0 = ki\ \ (A)\ \ (SnCl_4\,OCH_3^-) - k\text{-}i\ \ (D) - kii\ \ (D)\ \ (B)$$

$$(A) = (SnCl_4\,OCH_3^-)_o = (C)_o$$

$$(D) = \frac{ki\ \ (C)_o^{\,2}}{k\text{-}i + kii\ \ (B)}$$

The rate of progress of reaction which is observed as $-\frac{d(1)}{dt}$ is controlled by the rate of determining step

$$-\frac{d\,(1)}{dt} = kii\ (D)\ \ (B) \qquad \text{where} \qquad (B) \text{ is concentration of benzene}$$

$$= kii \quad \frac{ki\ \ (B)\ \ (C)^2}{k\text{-}i + kii\ \ (B)}$$

$$k - i \gg kii$$

$$\frac{d\,(1)}{dt} = k_1\ \ (C)^2 \qquad (B)$$

$$\text{where } k_1 = \frac{kii\ \ ki}{ki}$$

This result depends upon the fact that $(1)_o$ is greater than $(C)_o$. However in one of the experiments the concentration of catalyst is greater than that of monomer. Yet there is no deviation from second order kinetics with respect to catalyst. This is probably due to the formation of a mixture of 2:1 ($H^{(+)}$:DMPX) and 1:1 complexes at higher catalyst concentrations. The 2:1 complex affords two possible sites for reaction and will be more reactive than the 1:1 complex, accounting for the increase in rate observed. In accordance with the relationship:

$$-\frac{d(1)}{dt} = k_1 (C)^2 (B) \quad -4.4$$

a plot of rate of disappearance of (1) against $(C)^2$ was produced (Figure 4.11) and from the slope of this linear plot, taking benzene concentration into account, k_1 was found to be 2.25×10^{-3} moles^{-2} litres^2 sec^{-1}.

Figure 4.12 illustrates the application of equation 4.5 to the experimental data for the production of (111)

$$\frac{d(111)}{dt} = k_2 (11) (C) (B) \quad -4.5$$

The values for this plot (Table 4.12) were obtained from a number of experiments over wide range of concentrations of catalyst. The catalyst concentration may be estimated at any stage by assuming that one mole of catalyst is consumed for every mole of (11) produced and two moles for every mole of (111) produced. The values of $\frac{d(111)}{dt}$ were obtained by measuring the changing slope of the curves, shown earlier, from the plots of (111) against time. These measurements were confined to the early stages of reaction as changes in (111) become extremely small and difficult to estimate in the later stages. From the slope of the linear plot in Figure 4.12 a value of $k_2 = 4.44 \times 10^{-3}$ moles^{-2} litre^2 sec^{-1} may be deduced.

Figure 4.12 demonstrates that there may be considerable error in these measurements. The difficulties involved in accurately estimating small changes in (111) contribute to this error. Furthermore, the exact mechanism of the second reaction is difficult to postulate. Presumably protonation of the oxygen lone pair is the first stage of reaction as illustrated in Figure 4.13. Although protons are regenerated in the course of the first reaction and are available for protonation of the oxygen

TABLE 4.11

moles/litre $\times 10^2$	$\frac{d(l)}{dt} \times 10^5$	$(C)^2$ moles^2 litre^{-2}
8.8	1.72	7.74
7.0	1.33	4.90
5.6	0.10	3.14
3.4	0.56	1.49
2.0	0.12	0.40

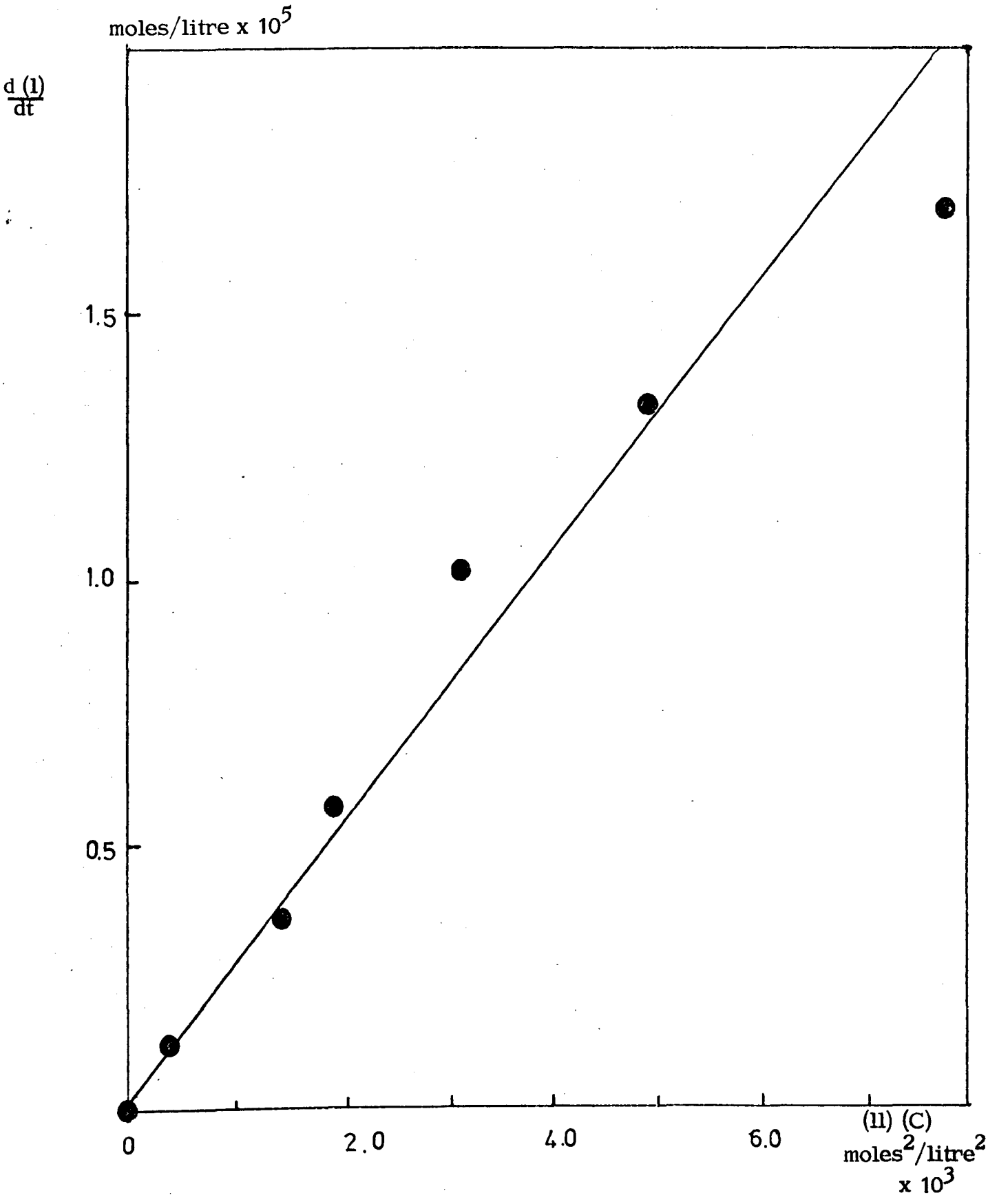

moles/litre x 10^5
$\frac{d(I)}{dt}$
1.5
1.0
0.5
0
2.0
4.0
6.0
(II) (C)
moles^2/litre^2
x 10^3

Figure 4.11

TABLE 4.12

(II) moles/litre x 10^3	(C) moles/litre x 10^2	d(III)/dt moles/litre/sec x 10^6	(II) (C) $moles^2$ $litre^{-2}$ x 10^4
14.0	4.80	3.34	6.72
15.0	4.41	2.21	4.54
10.1	5.60	2.22	5.66
4.0	4.01	1.66	1.66
9.0	3.6	1.21	3.22
6.2	3.41	1.01	2.11
5.0	1.50	0.20	0.75

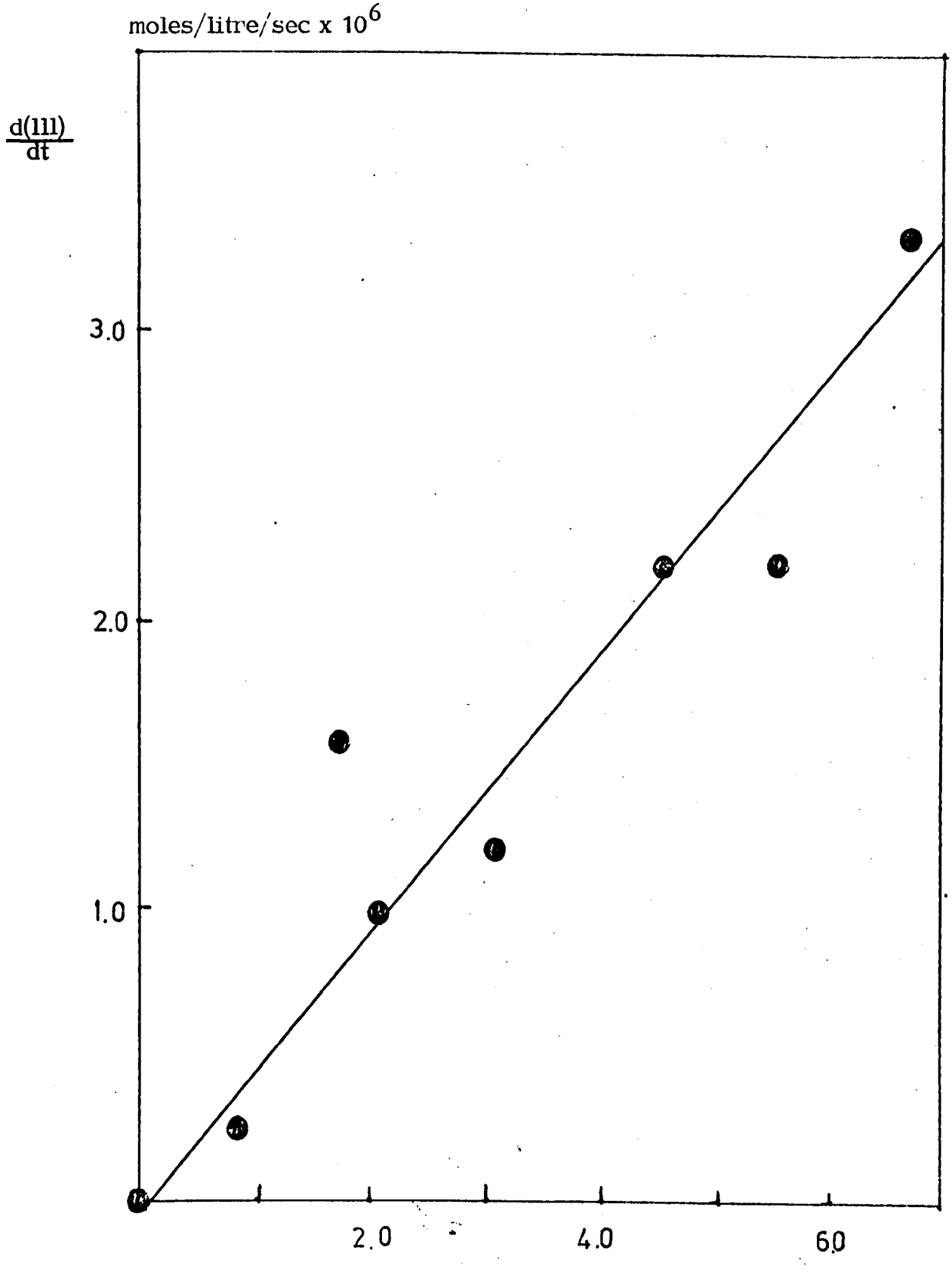

moles/litre/sec x 10^6
$\frac{d(III)}{dt}$
3.0
2.0
1.0
2.0
4.0
6.0
(II) (C)
moles^2 litre^{-2}

Figure 4.12

lone pair of electrons associated with the dimeric product (11) it is conceivable that there is competition for these protons by the monomer (1). This would mean that not all the dimer was available for reaction. Nevertheless the trend towards linearity noted in Figure 4.12 shows that the best approximation is to assume that protonation of the dimer occurs instantaneously upon its production. Despite the possible error in these results they may still serve for a useful qualitative comparison with values of rate constants obtained for the first two steps in the co-polymerisation of DCMB and benzene.

The values obtained for the DCMB system were measured using 1, 2 dichloroethane as a solvent and in order to compare these values closely with those obtained from the DMPX system, it was necessary to examine the latter system using 1, 2 dichloroethane as solvent. The dielectric constant of 1, 2 dichloroethane (10.23), is considerably less than that of nitromethane (35.9) and as ion separation, of the catalyst is proposed in the mechanism for the reaction in nitromethane it seems likely that kinetic examination in this solvent would become more complex owing to incomplete ion separation in the solvent of lower dielectric constant. In any case, the limited solubility of the polar catalytic complex in 1, 2 dichloroethane prevented kinetic measurements over a wide range of catalyst concentration and difficulties thus arise when measuring the order of reaction with respect to the catalyst. For these reasons only limited investigations were carried out in this solvent and the values listed in Table 4.14 were obtained by measuring the initial rate of reaction in 1, 2 dichloroethane and calculating the ratio of this rate to the rate of reaction in nitromethane measured using identical concentrations (Table 4.13).

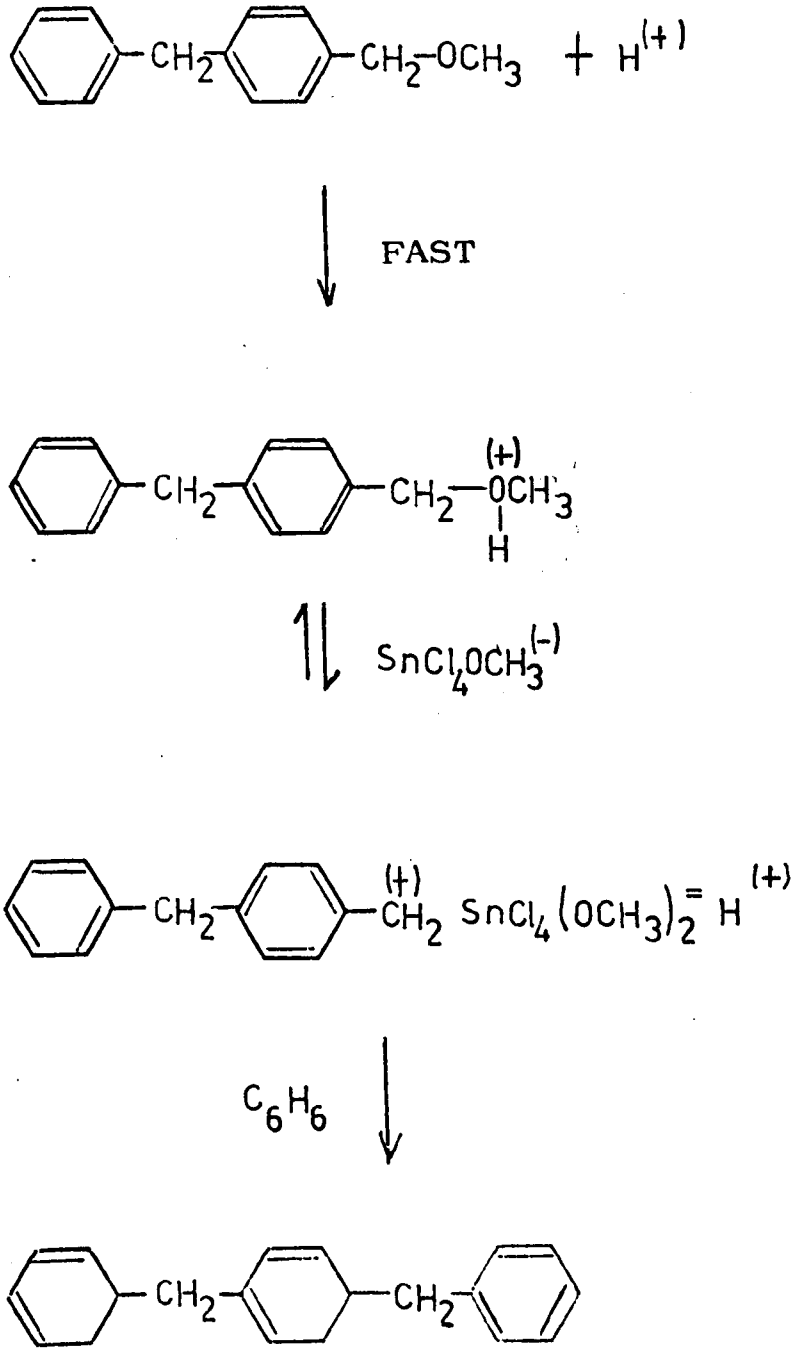

CH2
CH2–OCH3
+ H(+)
FAST
CH2
CH2
(+)
OCH3
H
SnCl4OCH3(-)
CH2
(+)
CH2
SnCl4(OCH3)2=
H(+)
C6H6
CH2
CH2

Figure 4.13

TABLE 4.13

Solvent	$(1)_o$ moles/litre x 10^2	$(C)_o$ moles/litre x 10^2	$(B)_o$ moles/litre	$\frac{d(1)}{dt_o}$ moles/litre/sec. x 10^6
CH_3NO_2	6.00	4.40	1.13	5.6
DCE	6.00	4.40	1.13	0.2

Values obtained for the first two rate constants of the DMPX and benzene co-polymerisation in nitromethane and DCE are listed together with those obtained for DCMB and benzene in Table 4.14.

4.4 Comparison of DMPX and DCMB Co-polymerisation

A kinetic examination of the first two stages of polymerisation of DCMB and benzene, reported by Grassie and Meldrum[16] has resulted in the mechanism outlined in Figure 4.14. First order kinetics have been demonstrated for the first reaction with respect to stannic chloride and DCMB. Figure 4.15 illustrates a typical plot of diminishing DCMB concentration against time. The linear plot observed in this case is in contrast to the curved plots obtained from similar experiments using DMPX as monomer. The acceleration in rate observed in the DCMB co-polymerisation is thought to be due to reaction of the monomer with the highly reactive aromatic products of this system. The contrasting inhibition effect observed in the DMPX co-polymerisation has been attributed, in chapter three to the complexing action of the methanol by-product to the tin nucleus of stannic chloride. The effect of hydrogen chloride, the condensation production of DCMB, upon the catalytic activity however has not been examined, although it has been shown on numerous occasions to act as a co-catalyst in Friedel Crafts polymerisations and this may partially account for the acceleration in rate observed in the DCMB co-polymerisation. Examination of the reaction kinetics using small amounts of hydrogen chloride in the reaction mixture would be necessary before the extent of this co-catalytic effect could be deduced.

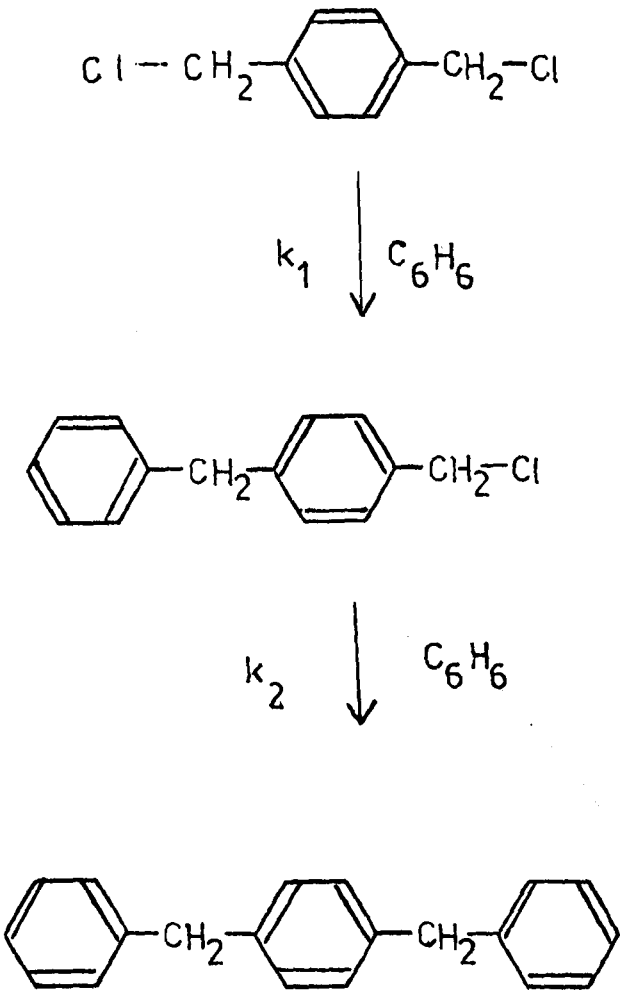


Figure 4.14

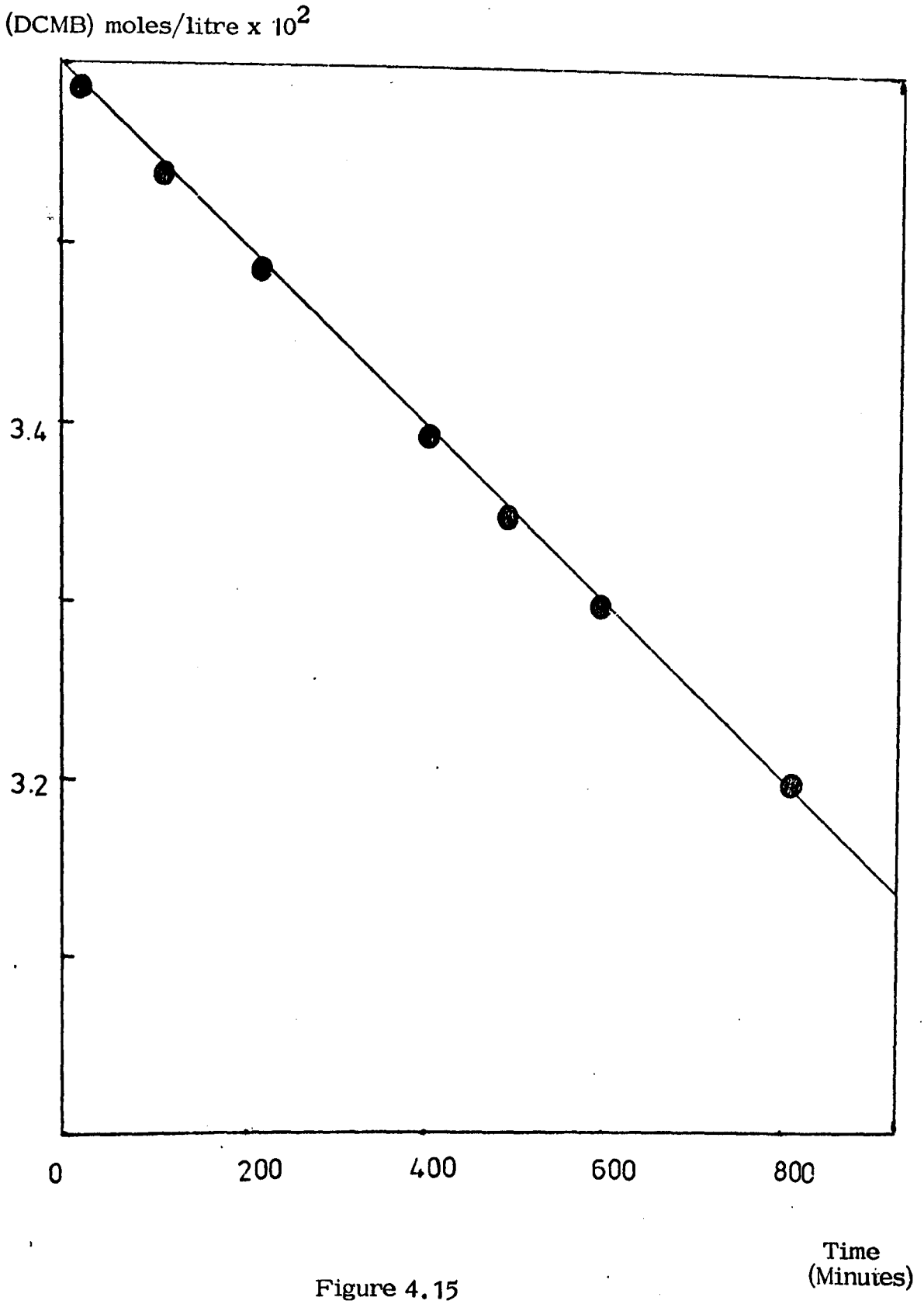


Figure 4.15

TABLE 4.14

Monomer	Solvent	k_1 moles^{-2} litre^2 sec^{-1}	k_2 moles^{-2} litre^2 sec^{-1}	Temperature ^oC
DMPX	CH_3NO_2	2.25×10^{-3}	4.44×10^{-3}	30
DMPX	DCE	8.16×10^{-5}	1.61×10^{-4}	30
DCMB	DCE	1.10×10^{-4}	1.30×10^{-3}	30

In view of the differences in the two mechanisms, the significance of any comparison of the absolute values of the rate constants for the two systems becomes less clear. However, it is interesting to compare the values of the ratios of k_2 to k_1 in each case. In the DCMB co-polymerisation the values of k_2/k_1 is 11.9. While in the DMPX system this value falls to 1.97. The absence of a strongly electronegative substituent in the dimer of the di(chlormethyl) benzene polymerisation facilitates separation of the chlorine atom in the formation of the complex and accounts for the very much higher value of k_2 as compared with k_1 in this case. The effect of replacing a methoxy group by an aromatic ring also appears to have the effect of facilitating the second reaction although this effect is smaller in this case. Grassie and Meldrum have also noted that the reactivity of the central aromatic nucleus of dibenzyl benzene (III) is greater than that of the two monosubstituted rings of this compound, confirming the observations of Olah[57] that increased substitution leads to greater reactivity of aromatic rings. This effect coupled with the high reactivity of the dimer of the DCMB polymerisation results in a high degree of branching in the polymer. In the DMPX system, the reactivity of the dimer is greater than that of the monomer but this effect is much less pronounced than in the DCMB polymerisation. The effect of solvents is discussed in chapter three.

It was envisaged that the differences observed by kinetic examination of the two co-polymerisations would affect the mechanism of polymer build up, the structure of the final high molecular weight material, and ultimately the thermal properties of these polymers. Subsequent investigations described in later chapters explore the exact nature of these effects.

CHAPTER 5

STRUCTURE OF POLYMERISATION PRODUCTS

5.1 Introduction

As mentioned in Chapter one, the overall objective of this investigation was to examine the mechanism and kinetics of a Friedel Crafts polycondensation reaction and to correlate this with structural and thermal analysis of the polymers produced. A possible mechanism for the reaction is proposed in Chapter four and it is now necessary to consider in detail the structural features of the polymer. This Chapter describes the structure elucidation of the first two products of polymerisation, which was essential before kinetic examination of the initial stages could be undertaken and in addition the main structural features of the high molecular weight polymer were deduced. Subsequent chapters relate these structural features to the mechanism of polymerisation and to the thermal properties of the polymer.

5.2 Structure of the First Two Products

The structures of the first two products are elucidated by first examining a low conversion reaction mixture by GLC and GCMS, before infrared and NMR spectra of products, isolated by preparative TLC, were examined.

Table 5.1 and Figure 5.1 show retention times and molecular weights of the three components present in a low conversion reaction mixture obtained by the use of GCMS. Each of these compounds was then isolated by preparative TLC. Figure 5.2 illustrates the infrared spectrum of P_1 which is identical in all respects to the infrared spectrum of a known sample of DMPX (1). In addition the NMR spectrum (Figure 5.3, Table 5.2) is identical to that of DMPX showing three main singlet absorptions at 2.65 τ , 5.57 τ and 6.62 τ . The singlet nature of each peak indicates the symetry of the molecule with four equivalent aromatic protons showing resonance at 2.65 τ , four equivalent methylene protons at 5.57 τ deshielded by the neighbouring oxygen atoms and aromatic ring and six methyl protons at 6.62 deshielded by neighbouring oxygen atoms. The molecular weight, obtained from GCMS, of 166 confirms that P_1 is due to unreacted monomer.

Figure 5.4 illustrates the infrared spectrum of P_2 which is similar to that of DMPX but differing in several features including absorptions at 690 and 730 cm^{-1} which may be attributed to out of plane deformations characteristic of a monosubstituted aromatic ring. Figure 5.5 illustrates the NMR spectrum of P_2 and the data is listed in Table 5.3 The NMR, infrared, and GCMS evidence is consistent with the identification of P_2 as dibenzyl methyl ether (DBME) (11) (Figure 5.8) which is the first product likely to arise from reaction of benzene and DMPX in the presence of stannic chloride. The NMR spectrum is more complex than that of DMPX due to the lack of symetry of the dimeric molecule. The complex pattern observed between 2.6 and 2.9 τ , with a major peak at 2.85 τ is attributed to resonance of aromatic protons. The methylene protons which are adjacent to an oxygen atom absorb at 5.57 while those situated between the aromatic rings absorb at 6.01 τ . The three methyl protons absorb at 6.625 τ .

TABLE 5.1

Component	Retention Time (Min.)	Molecular Weight
P_1	20	166
P_2	28	212
P_3	36	258

Figure 5.1

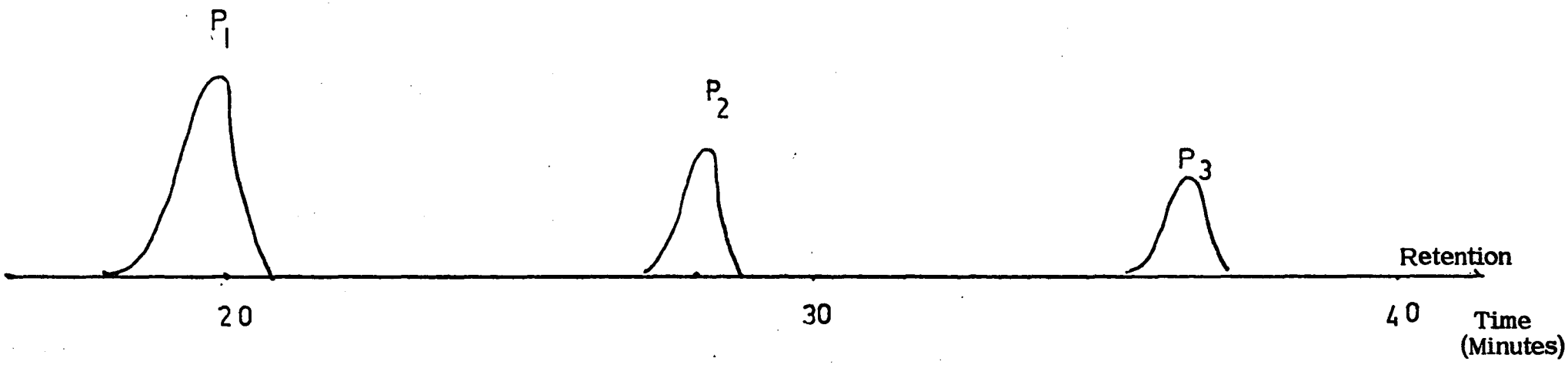


TABLE 5.2

(NMR Data from P_1)

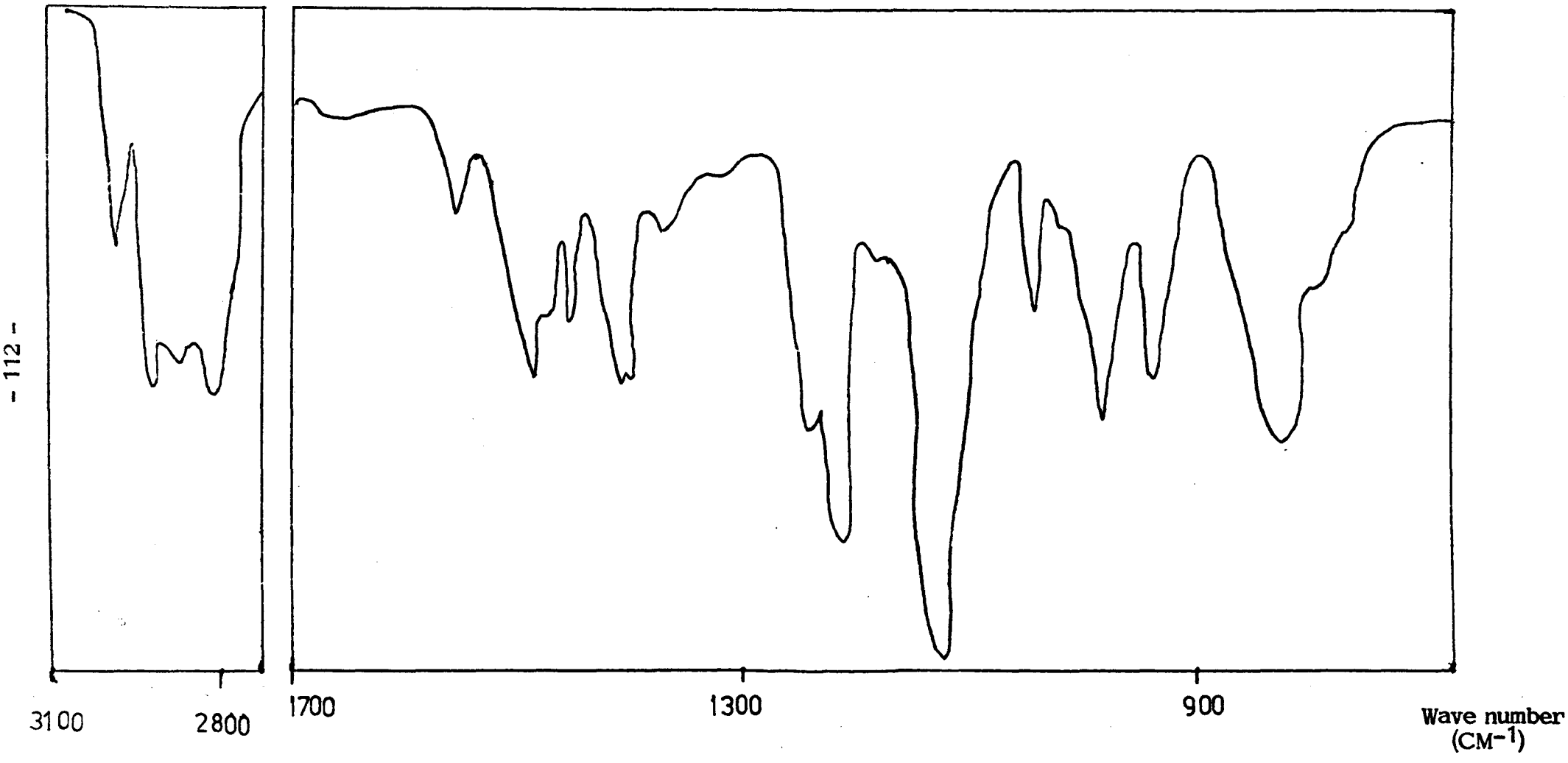
Value	Nature of Peak	Integration
2.65	Singlet	4
5.57	Singlet	4
6.62	Singlet	6

TABLE 5.3

(NMR Data for P_2)

Value	Nature of Peak	Integration
2.75	Complex	9
5.57	Singlet	2
6.01	Doublet	2
6.62	Singlet	3

Figure 5.2



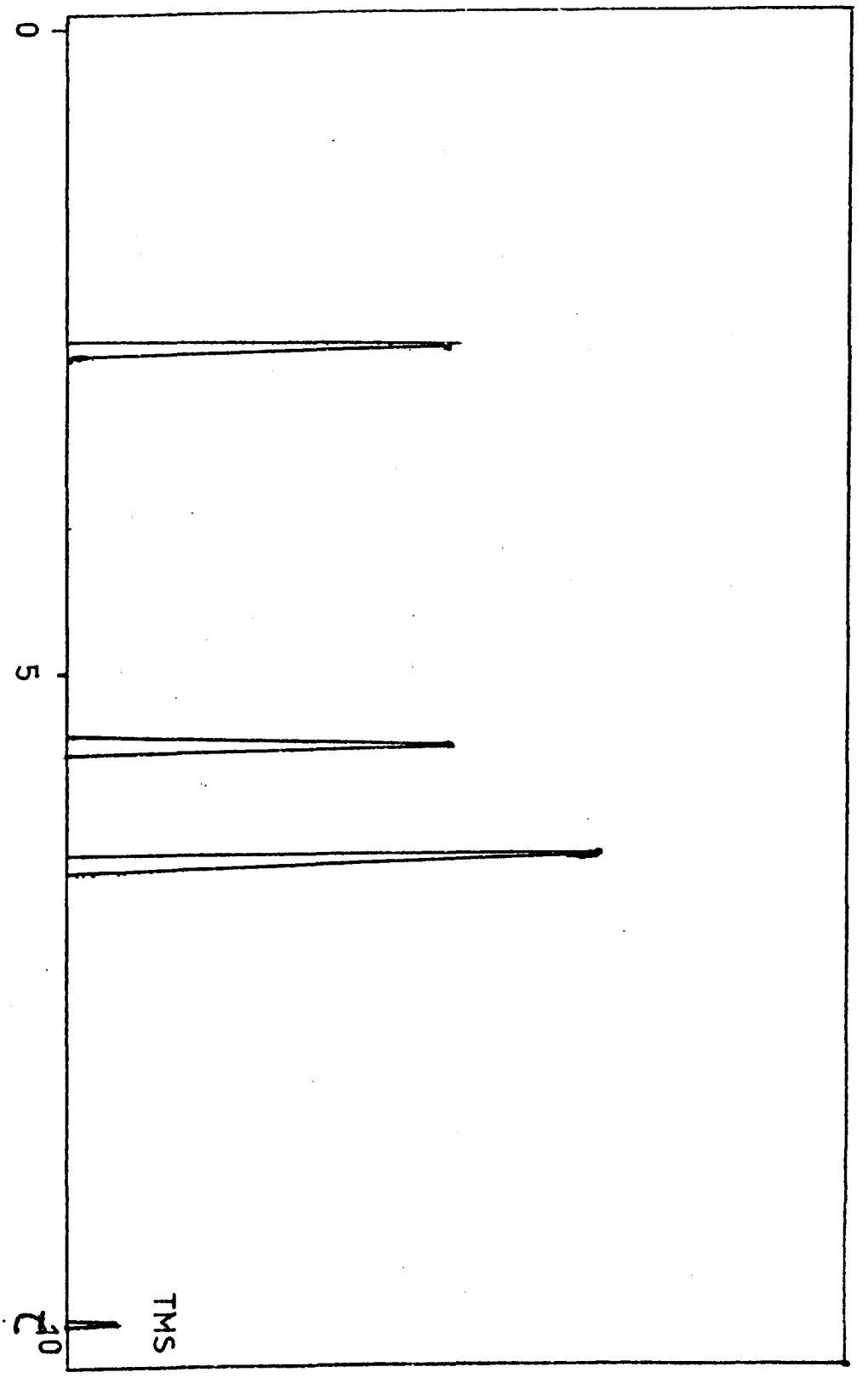
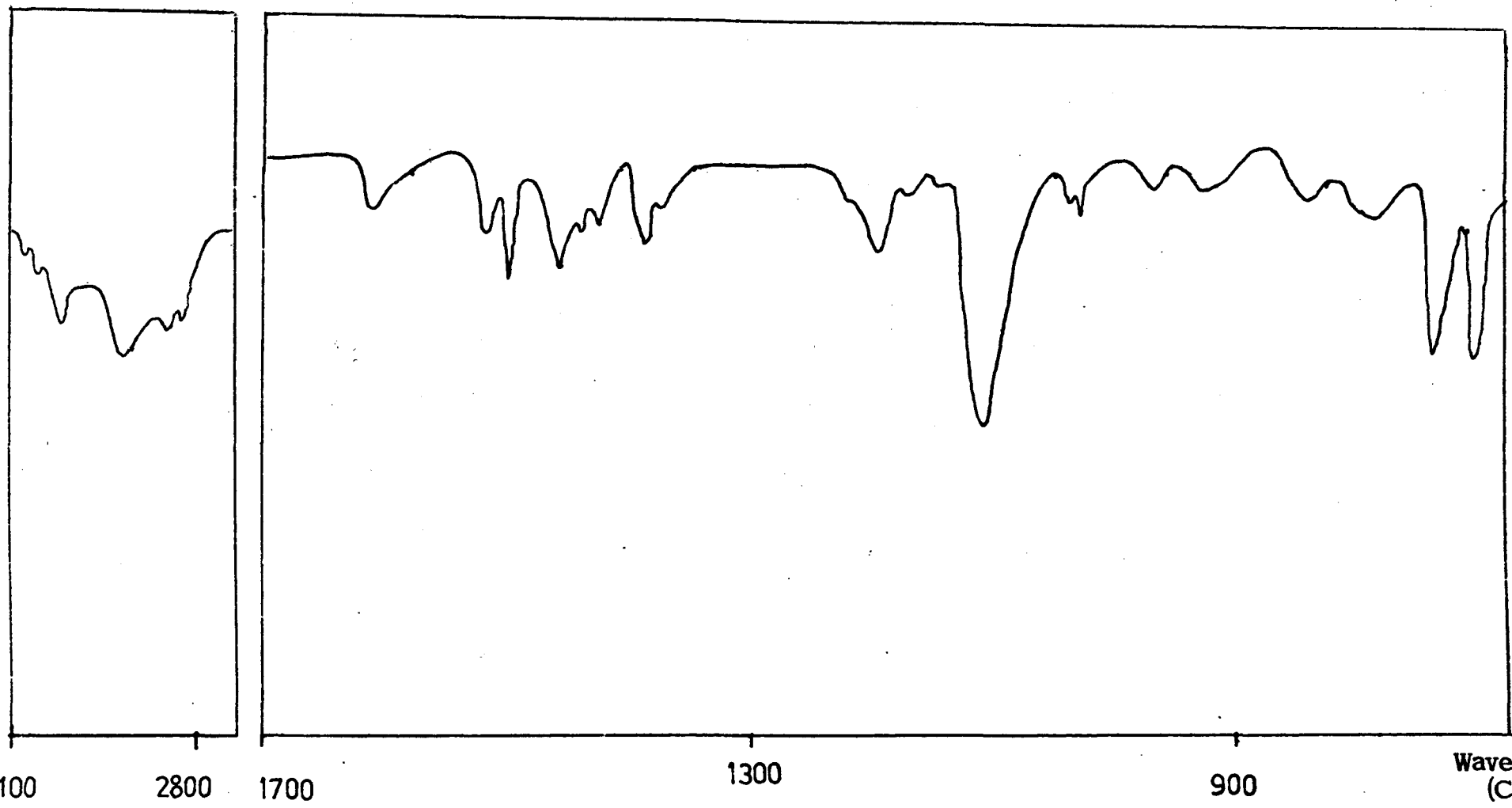


Figure 5.3

Figure 5.4



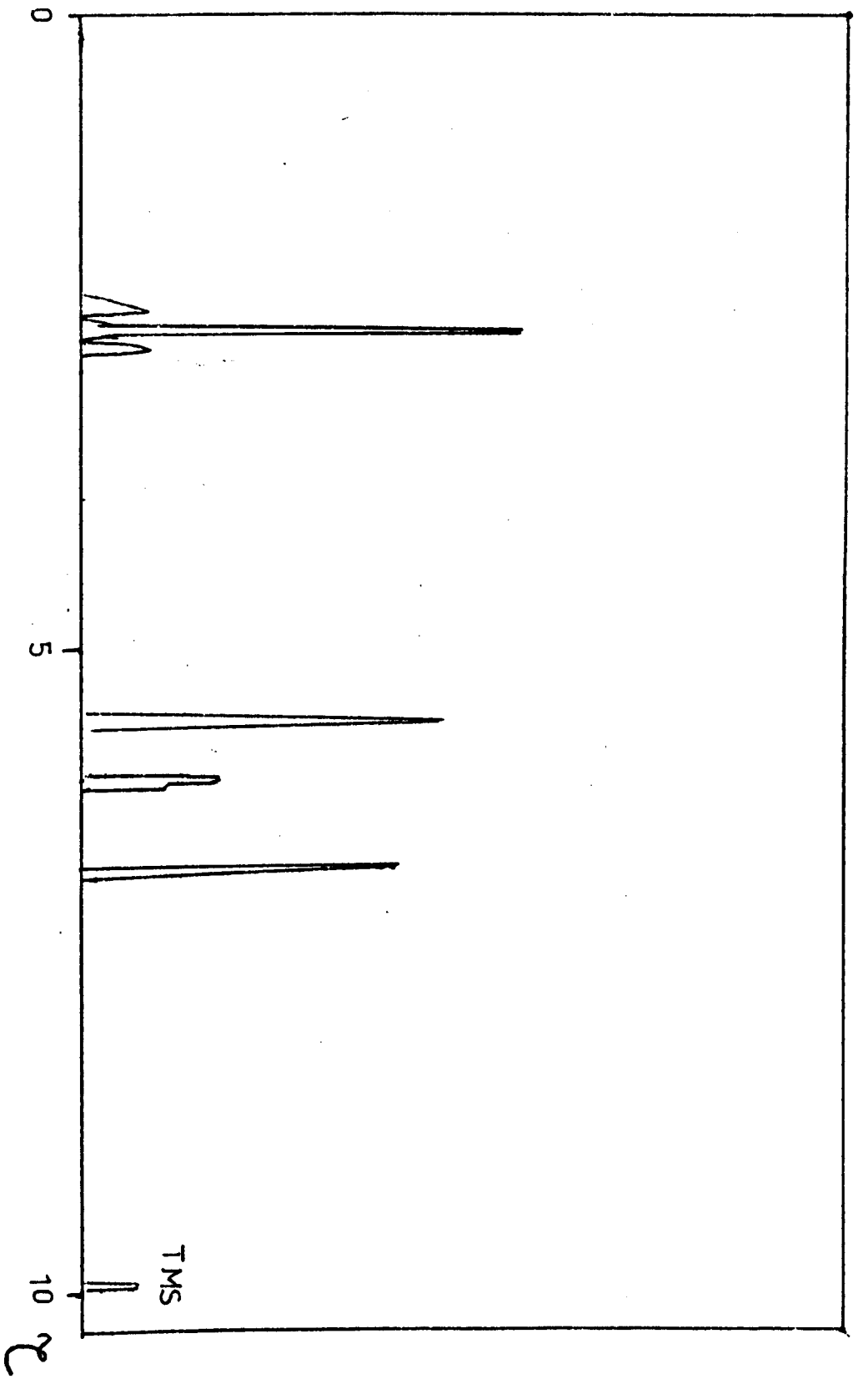


Figure 5.5

Figure 5.6

TABLE 5.4

(NMR Data for P_3)

Value	Coupling	Integration
2.75	Singlet	10
2.90	Singlet	4
6.05	Doublet	4

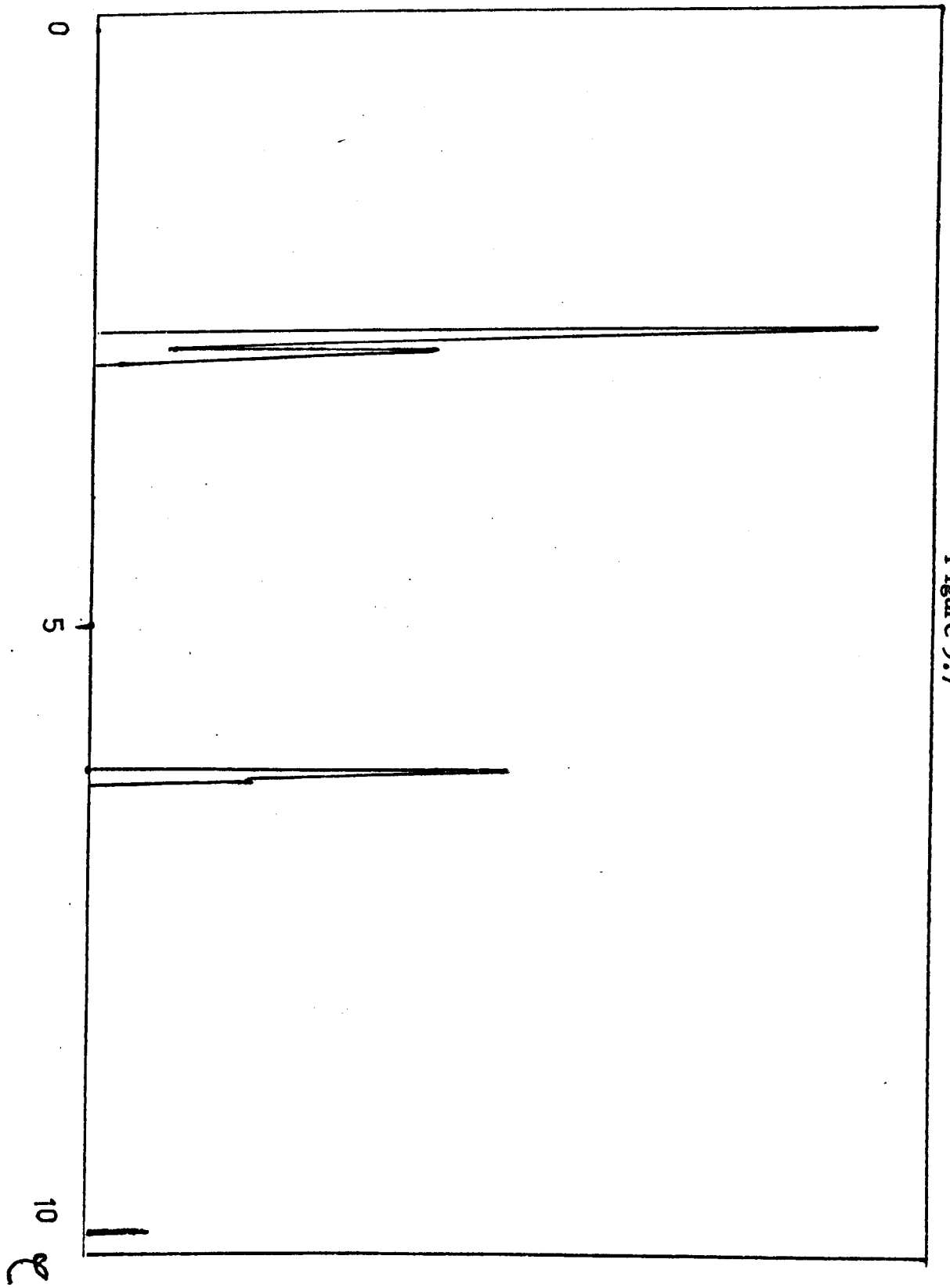
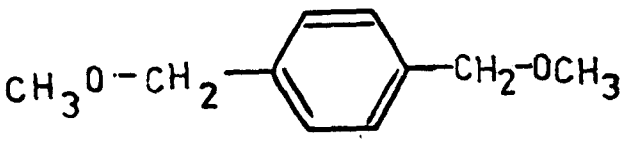
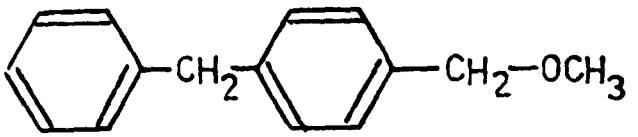


Figure 5.7

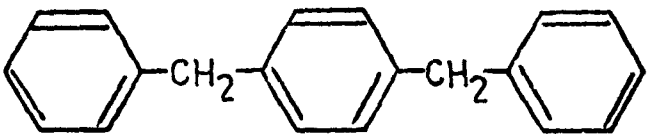
Figure 5.8



(I)



(II)



(III)

From the GCMS, infrared and NMR data, P_3 was identified as dibenzyl benzene (111) (Figure 5.8) which results from reaction of benzene and DBME (11). GCMS reveals a molecular weight of 258, while the infrared spectrum indicates the presence of di- and mono-substituted aromatic rings (Figure 5.6). The absorption maximum at 2.75 integrating for ten protons is undoubtedly due to the two monosubstituted periphereal aromatic rings, while the central aromatic ring results in absorption at 2.9 τ. Resonance at 6.1 τ for four protons may be attributed to the methylene protons which are situated between the rings. (Figure 5.7)

5.3 Structure of Polymers Derived from DMPX

As discussed fully in Chapter one, the structure of polybenzyls has been the subject of much controversy[15-23, 34-36], and considerable doubt still exists as to the extent of branching in these polymers. Much of the evidence cited in support of the structures proposed by previous workers has been based on infrared spectroscopy but little investigation has been carried out by NMR. The solubility of polymers produced from DMPX allows NMR analysis of their structure and this was envisaged as a useful technique in the determination of the structural features of the polymer molecule. In addition the spectral data obtained from the low molecular weight products (11) and (111) and from the monomer (1) could be used as a convenient model thus facilitating structure elucidation of the high polymer. Also infrared analysis of both the soluble and insoluble protons of the polymeric material allowed comparison between the two.

Figure 5.9

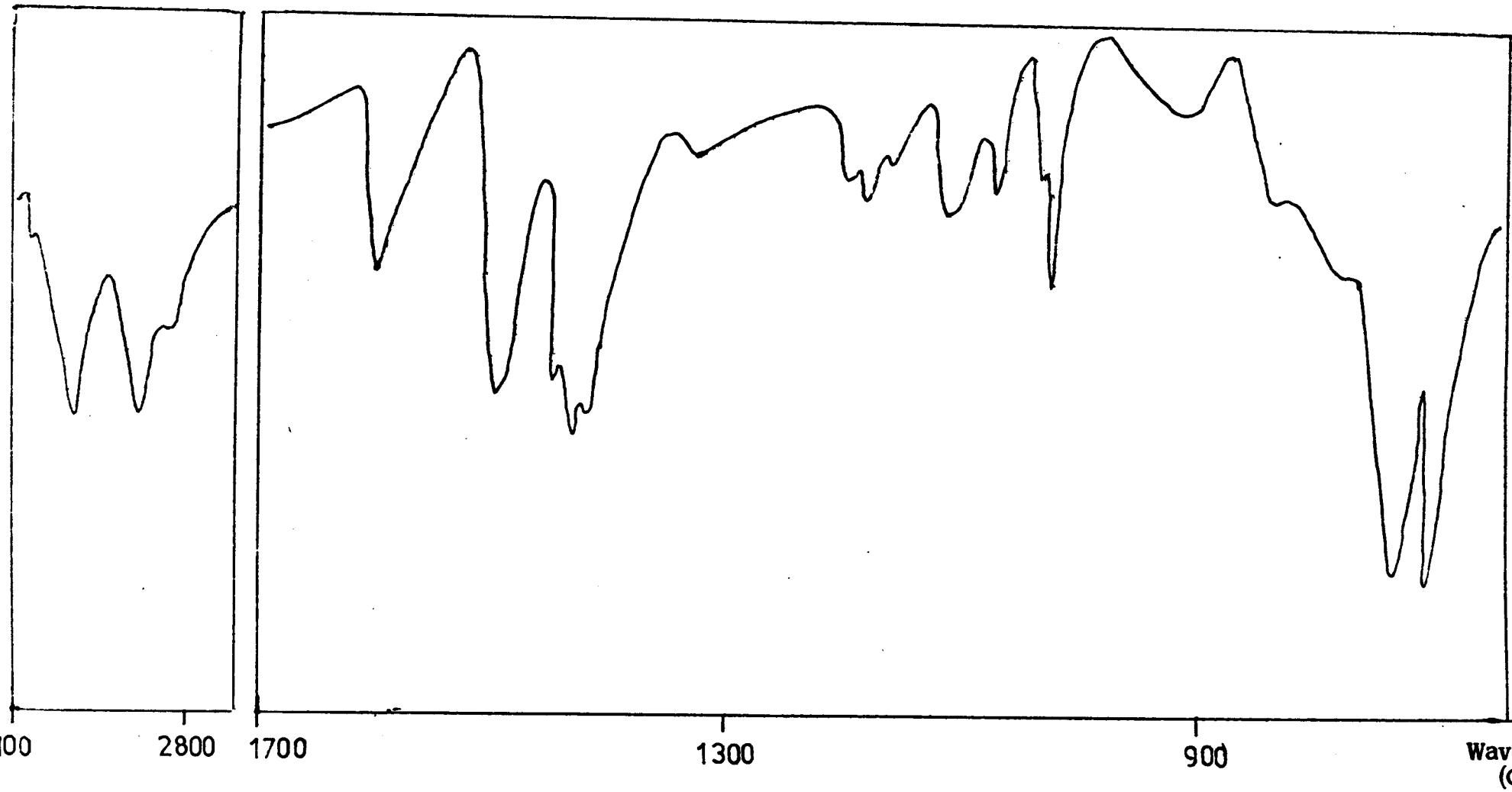
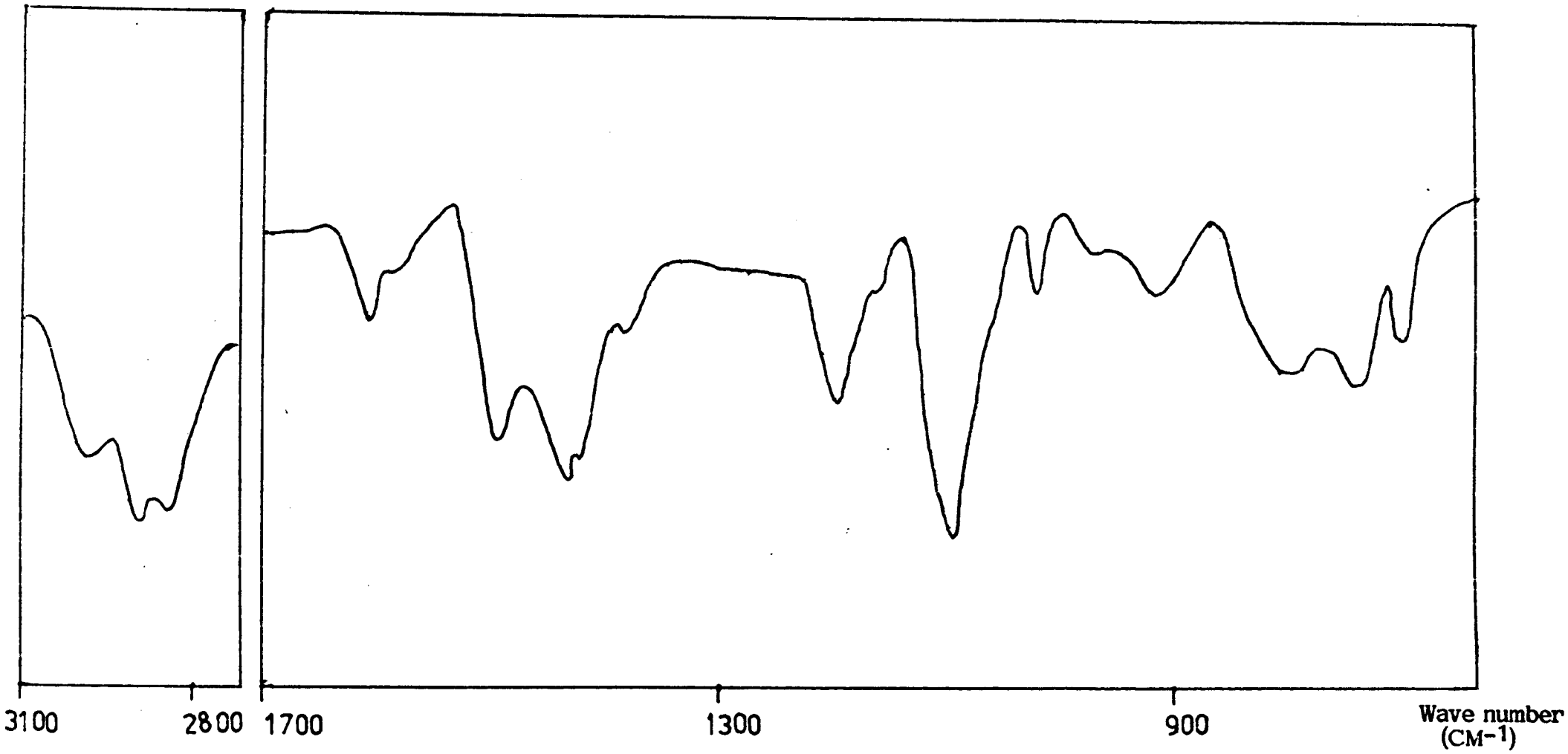


Figure 5.10



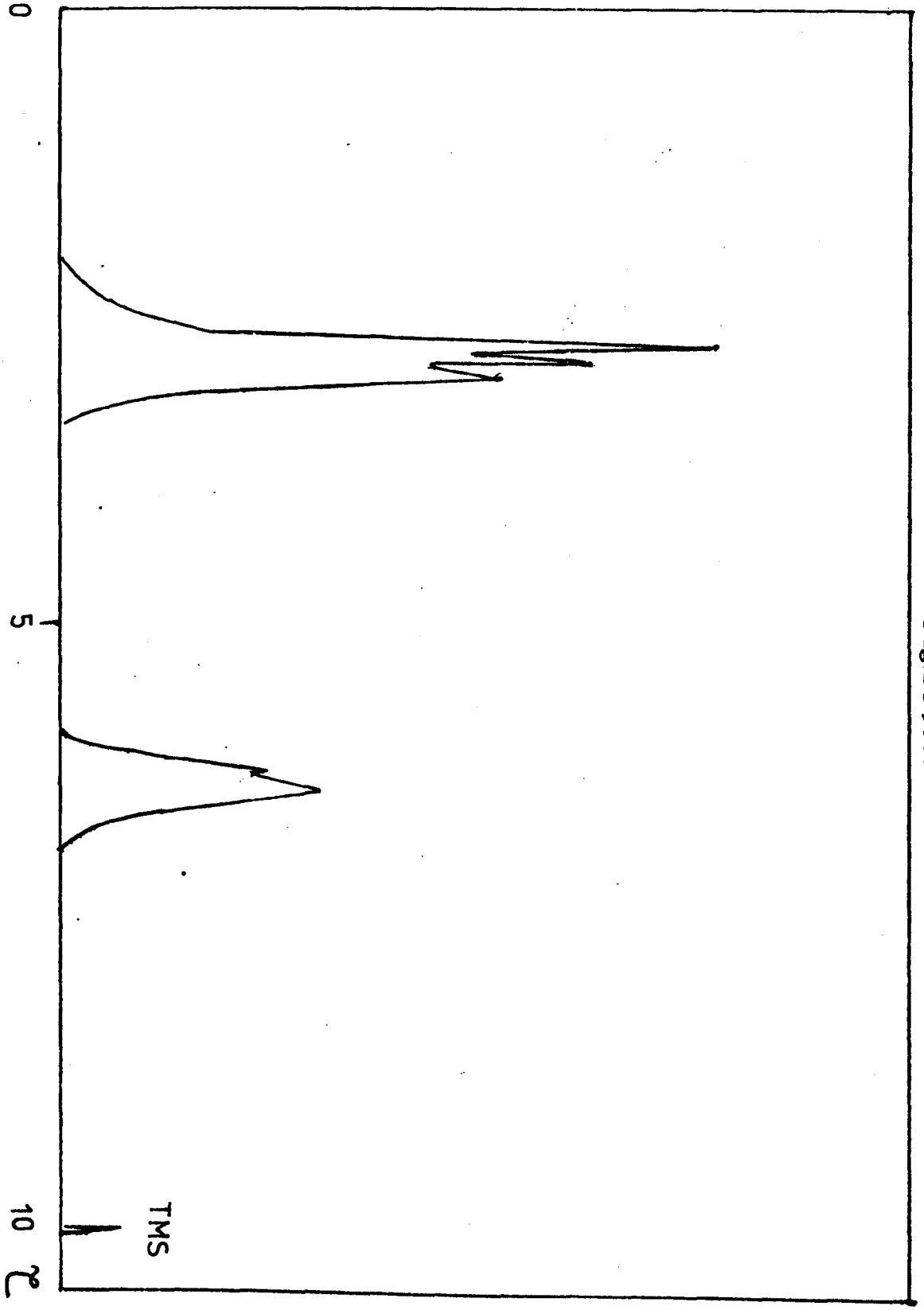


Figure 5.11

a) Infrared Spectrum of Soluble Polymer

Figure 5.9 illustrates the infrared spectrum of a soluble co-polymer of molar feed ratio 5:1 (Benzene: DMPX). Absorptions at 690 cm^{-1} and 730 cm^{-1} indicate the presence of a large number of monosubstituted aromatic rings while absorption in the 790-850 cm^{-1} region is due to the presence of disubstituted aromatics.

b) Infrared of Insoluble Polymer

Figure 5.10 illustrates the infrared spectrum of the insoluble portion of a benzene-DMPX copolymer (5:1 benzene:DMPX molar feed ratio). The spectrum is in many ways similar to that of the soluble polymer but by contrast absorption is less at 690 and 720 cm^{-1} but greater around 800 cm^{-1}, indicating a greater degree of aromatic substitution.

c) NMR of Soluble Polymers

The NMR spectrum of co-polymers of DMPX and benzene using a variety of molar feed ratios were recorded together with the spectrum of the DMPX homopolymer. Figures 5.11, 5.12 and 5.13 illustrate the NMR spectra of co-polymers of molar feed ratio 5:1, 2.5:1 and 1:1 (Benzene:DMPX) respectively while Figure 5.4 illustrates the NMR of the DMPX homopolymer. The NMR spectrum of the 5:1 τ copolymer reveals absorption maxima at 2.8τ , 2.9τ and 3.1 and at 6.0τ . Resolution in the spectra of high molecular weight material is poorer than that of the low molecular products (II) and (III) and the chemical shift values and integration of the peaks cannot be determined with corresponding accuracy. Nevertheless, it is reasonable to propose that the absorptions at 2.8τ and 2.9τ are due to the presence of mono- and di-substituted aromatic rings, by comparison with absorption at 2.75 and 2.90τ in dibenzyl benzene (III). Resonance which occurs at 3.1 is consistent with known τ values for tri-substituted rings. Using a

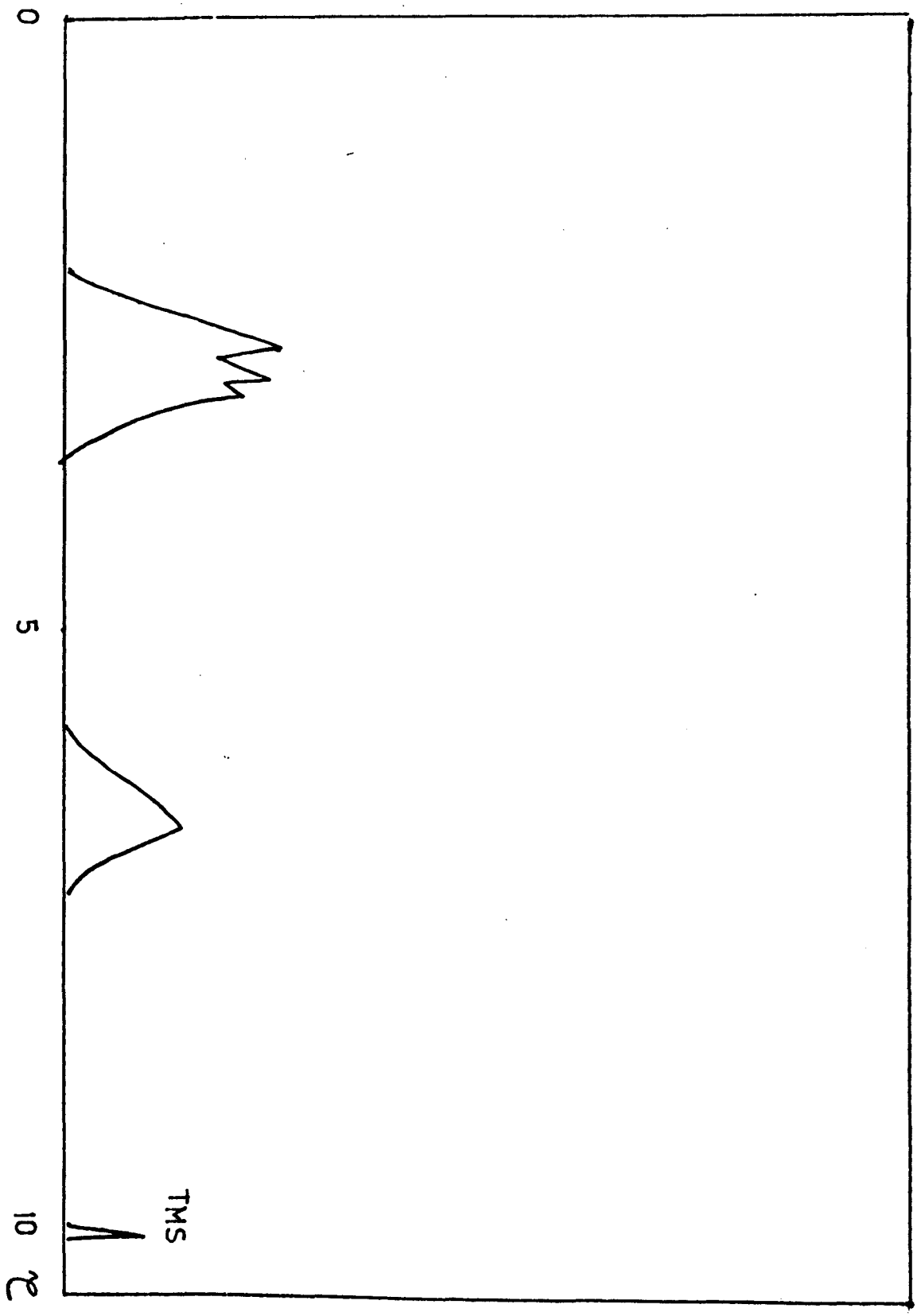


Figure 5.12

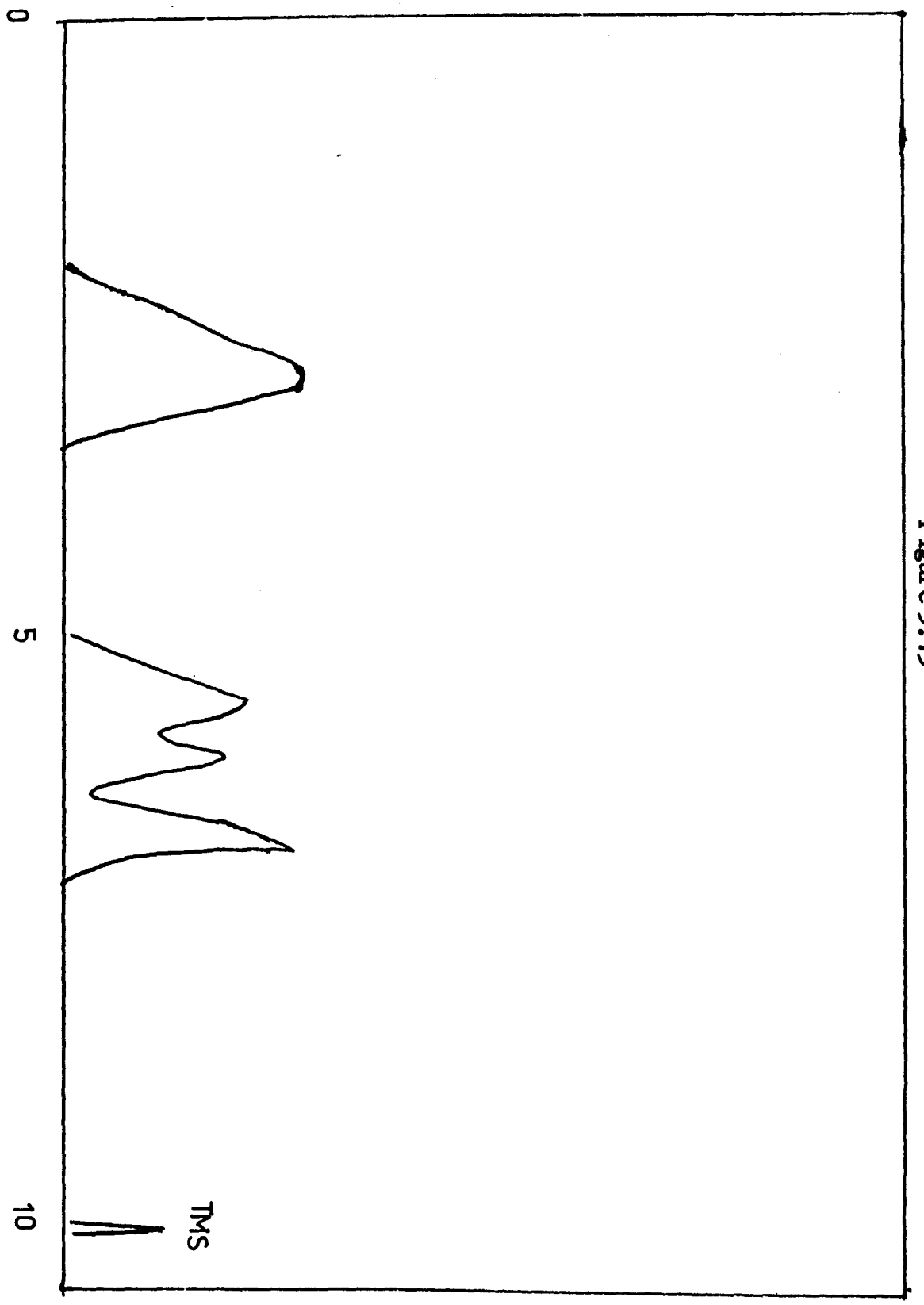


Figure 5.13

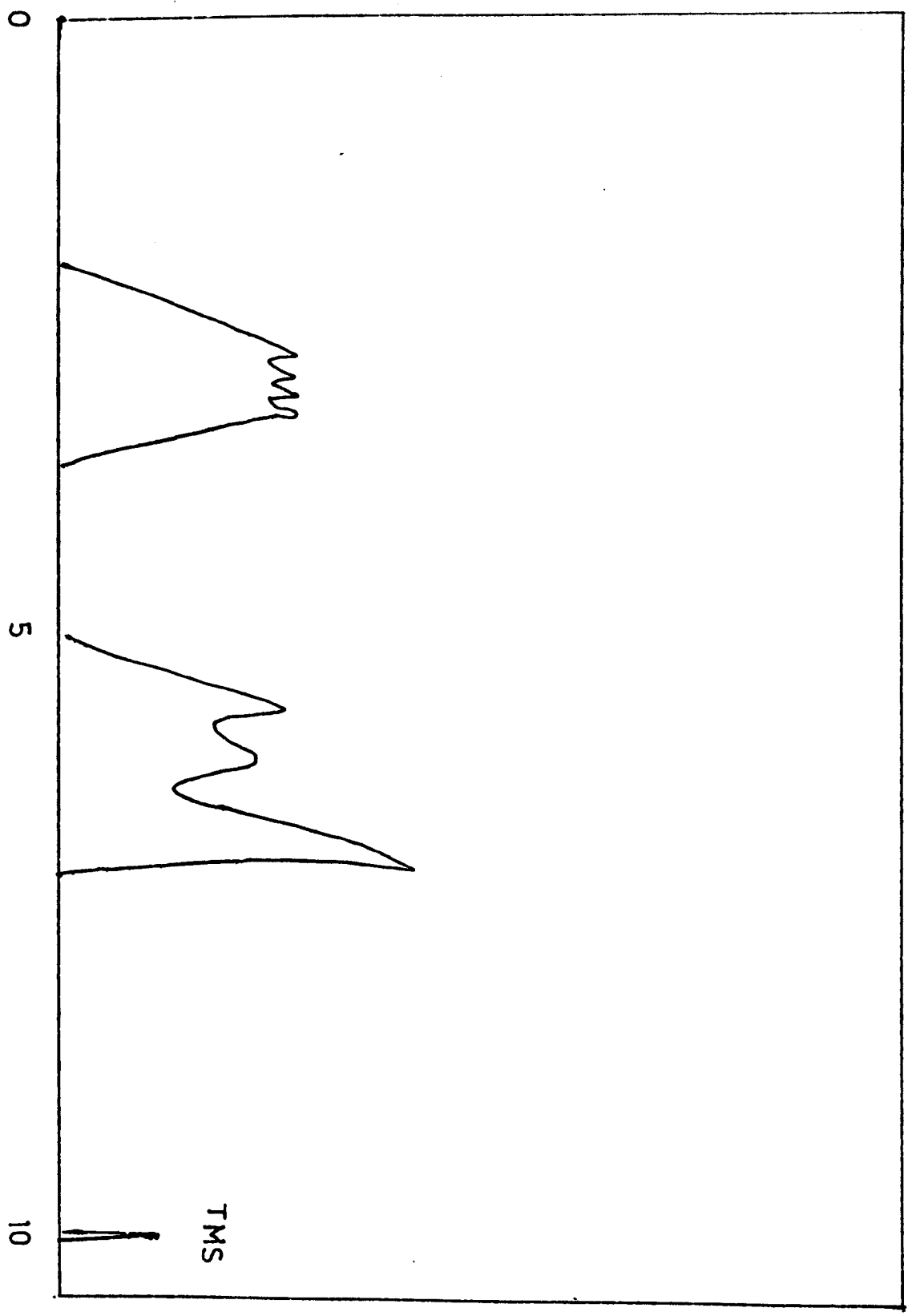


Figure 5.14

frequency of 60 MHz it was not possible to obtain an accurate integration ratio of these peaks and although the use of the 100 MHz instrument improved resolution, overlap of the peaks was still considerable and accurate estimation of their areas was not possible. However, qualitatively, it could be said that the peak whose maximum is at 2.8 τ is slightly larger than that at 2.9 τ which in turn occupies a slightly larger area than that at 3.1 τ. If the concentration of mono-, di- and tri-substituted rings in the polymer is equal then the theoretical value of the ratio of the peaks due to aromatic protons should be 5:4:3 and inspection of the three peaks of the spectrum due to aromatic protons reveals that this would be a reasonable value. It is therefore reasonable to propose that the number of mono-, di and tri-substituted aromatic rings is approximately equal in the polymer. The large number of mono- and tri-substituted rings which are clearly present in the polymer excludes the possibility of a linear structure. A branched structure similar to that depicted in Figure 5.15 is therefore proposed. The equal number of monosubstituted aromatic rings and disubstituted rings indicates that these branches must be short and that in the central core of the polymer which is surrounded by periphereal benzene rings, the average degree of substitution must be 2.5. The absence of resonance at 6.0 τ indicates that the concentration of unreacted methoxyl groups in the polymer must be very small. Thermal studies of this copolymer which are described in Chapter six, have revealed that methoxyl groups are present in low concentrations, however.

The integration ratio of aromatic protons (2.8-3.1 τ) to aliphatic protons(6 τ) is 2.2. If the number of monosubstituted aromatic rings is equal to that of di- and tri-substituted rings then the average number of aromatic protons associated with each ring will be four. In high molecular weight polymer, the total number of aromatic rings should be equal to the number of methylene groups and the ratio of the two types of protons should thus be two which is close to the value found.

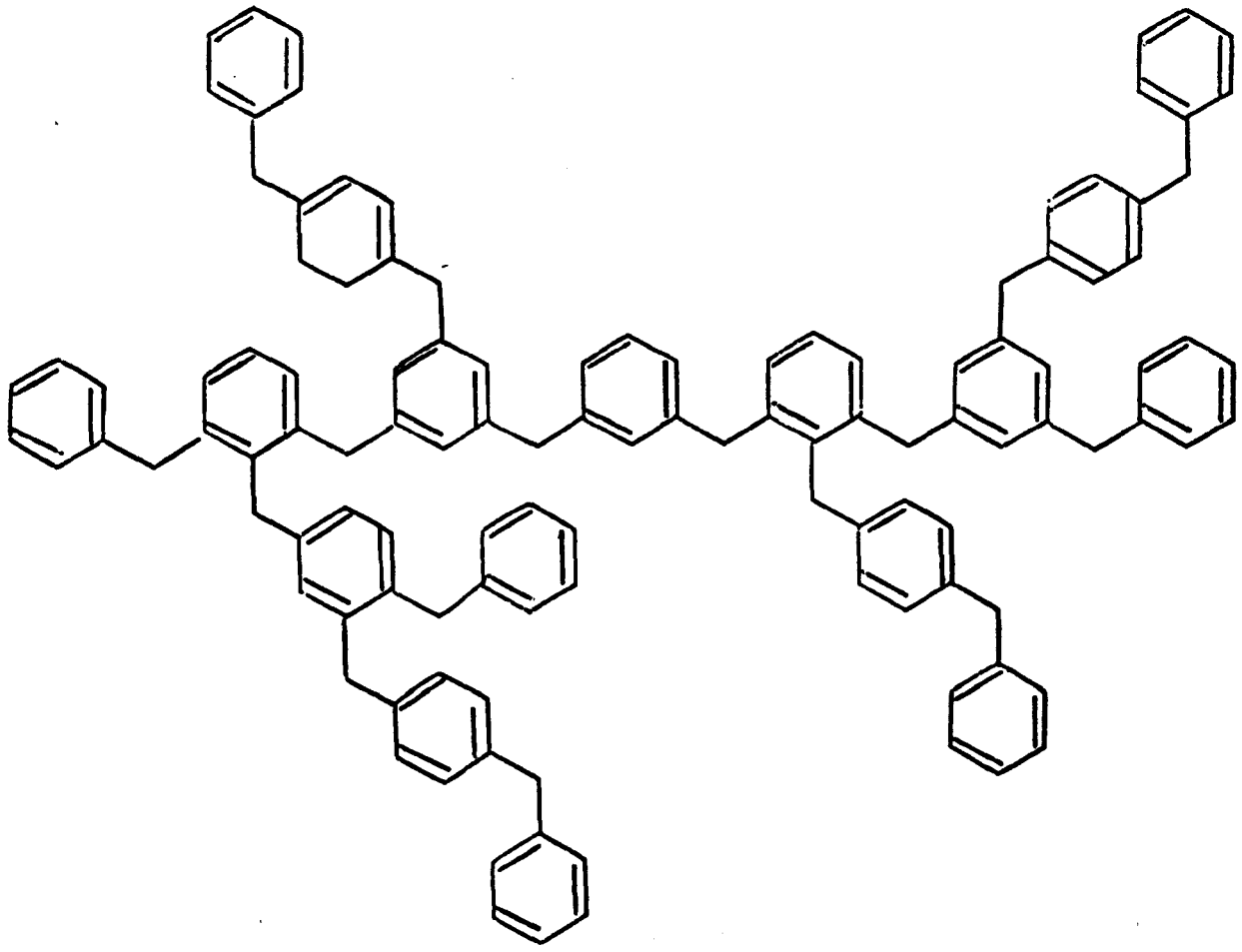


Figure 5.15

Structure of polymers based on DMPX

The NMR spectrum of the 2.5:1 copolymer is illustrated in Figure 5.2. The resolution of the peaks due to aromatic protons is again insufficient for accurate integration but it may be qualitatively noted that the ratio of mono-, di- and trisubstituted rings is similar to the ratio observed for the 5:1 copolymer. In addition no absorption is noted at 6.6τ indicating the apparent absence of methoxyl groups. No significant difference is therefore apparent in the spectra of these two copolymers.

The NMR spectrum of the 1:1 copolymer (Figure 5.13) shows a broad absorption between 2.9 and 3.1τ due to aromatic protons and absorption at 6.0τ due to methylene protons situated between aromatic rings. In addition resonance at 6.6τ indicates the presence of methoxyl groups in considerable concentration as does the absorption at 5.57τ (cf NMR of (11) Figure 5.5). The integration ratio of aromatic protons to protons at 6.6τ is 1.73 indicating that a considerable concentration of methoxyl groups is present in the polymer. The NMR spectrum of the homopolymer (Figure 5.14) is in many ways similar to that of the 1:1 copolymer, although the concentration of methoxyl groups is slightly greater as the value of the ratio of aromatic to protons at 6.6τ falls to 1.48.

5.4 Discussion

From the infrared and NMR evidence which is discussed above, it is clear that the soluble portion of polymer consists of a central core of di- and tri-substituted aromatic nuclei surrounded by a periphery of pendant benzene rings at the end of short chain branches. By contrast, the infrared spectrum of the insoluble polymer reveals that monosubstituted nuclei are present in lower concentrations and it is likely that this is due to crosslinking between the chains of the

polymer similar to the situation found in polymers derived from DCMB.

The degree of substitution in polymers derived from DMPX is somewhat less than that proposed by previous workers. Parker[36], for example, has proposed that the average degree of substitution in aromatic nuclei in homopolymers of chloromethyl benzene is three whereas the present investigation has shown this value to be 2.5 in copolymers of DMPX and benzene. Kinetic examination by Parker and Davies of the self polymerisation of chloromethyl benzene and of copolymerisation of DCMB to benzene by Grassie and Meldrum[16] have shown that the dimeric products of each of the two systems are more reactive than the monomers by a factor of ten. In addition the NMR data in the present work has shown that the central aromatic nucleus in dibenzyl benzene has a greater field of electron density as the chemical shift associated with this ring occurs at a higher field (2.9 τ) than that due to the adjacent aromatic rings (2.75 τ). From this it is reasonable to propose that aromatic nuclei in the central core of the polymer are highly activated towards aromatic substitution. This feature coupled with the very high reactivity of pendant chloromethyl groups associated with oligomeric products should therefore result in long chain branches. Highly reactive chloromethyl groups in the polymer chain should also promote crosslinking between the polymer chains.

Kinetic examination of the copolymerisation of DMPX and benzene described in Chapter four, has shown that in this system, the dimer is only twice as reactive as the monomer. As a consequence, the oligomeric products of condensation are less reactive and branching of these molecules to aromatic nuclei is less favoured. This accounts for the short branches present in the DMPX copolymer as branching by the monomer addition as opposed to oligomer addition becomes more favourable. The

lower reactivity of the pendant methoxyl group would also account for the smaller degree of crosslinking in DMPX polymers and thus greater solubility as compared with those derived from DCMB.

The structural data in conjunction with kinetic analysis correlates well with the results of Harris[14] who has noted that pre-polymers derived from DCMB crosslink easily upon heating while those from DMPX require the use of a crosslinking agent. The high reactivity of the pendant chloromethyl group as compared with pendant methoxyl group is now proposed as a reason for this observation.

CHAPTER 6

THERMAL DEGRADATION OF RELATED FRIEDEL CRAFTS POLYMERS

6.1 Introduction

The preceeding chapters have described kinetic analysis of co-polymerisations based on DMPX and the elucidation of the main structural features of the polymers produced. These structural features have been correlated with the results of kinetic analysis and it now remains to relate these structural features to the thermal stability of the polymer.

The structure of these polymers, in particular the degree of branching and crosslinking, varies according to the nature of the bifunctional monomer and aromatic co-monomer from which they are derived and the molar feed ratio of monomer to co-monomer used for polymerisation. It was envisaged that the degree of branching and crosslinking in these polymers would influence their stability, and for this reason thermal volatilisation analysis (TVA), in conjunction with thermal gravimetric analysis (TGA), was carried out on polymers of DMPX and benzene derived from varying molar feed ratios. The break-down patterns and degradation products of these copolymers were examined.

6.2 Preparation of Polymers

All polymers used in this investigation were prepared under nitrogen using 1, 2 dichlorethane as solvent as described in Chapter two. This proved to be the most effective means of obtaining large amounts of high molecular weight material. The infrared spectra of the polymers prepared under nitrogen were identical with those of the polymers produced under vacuum so it was concluded that their structures are identical.

6.3 Molecular Weights

The molecular weights of the polymers used for thermal analysis were all in the region of 5000, measured using vapour pressure osmometry. It was not possible to estimate the molecular weights of the insoluble portion of polymer.

6.4 Thermal Volatilisation Analysis (TVA) of Various Copolymers

Thermal degradations using TVA were carried out under vacuum at a programmed heating rate of 10^{o}/min. in all cases as described in Chapter two.

Traces were obtained which showed the degradation patterns of soluble and insoluble portions of polymers prepared using a variety of molar feed ratios of DMPX and benzene. A TVA thermogram of the DMPX homopolymer was also obtained. Figure 6.1 illustrates the TVA trace of a soluble copolymer prepared using a molar feed ratio of 5:1 (Benzene:DMPX). It is identical to that obtained from a copolymer using 10:1 molar feed ratios. Each has a single peak, which is due to volatile products which include a large proportion of components which are non condensable at all cold trap temperatures. This is indicated by the response of the Pirani which is situated after the 196^{o}C trap. The onset of volatilisation occurs at 368^{o}C while the maximum rate of evolution of

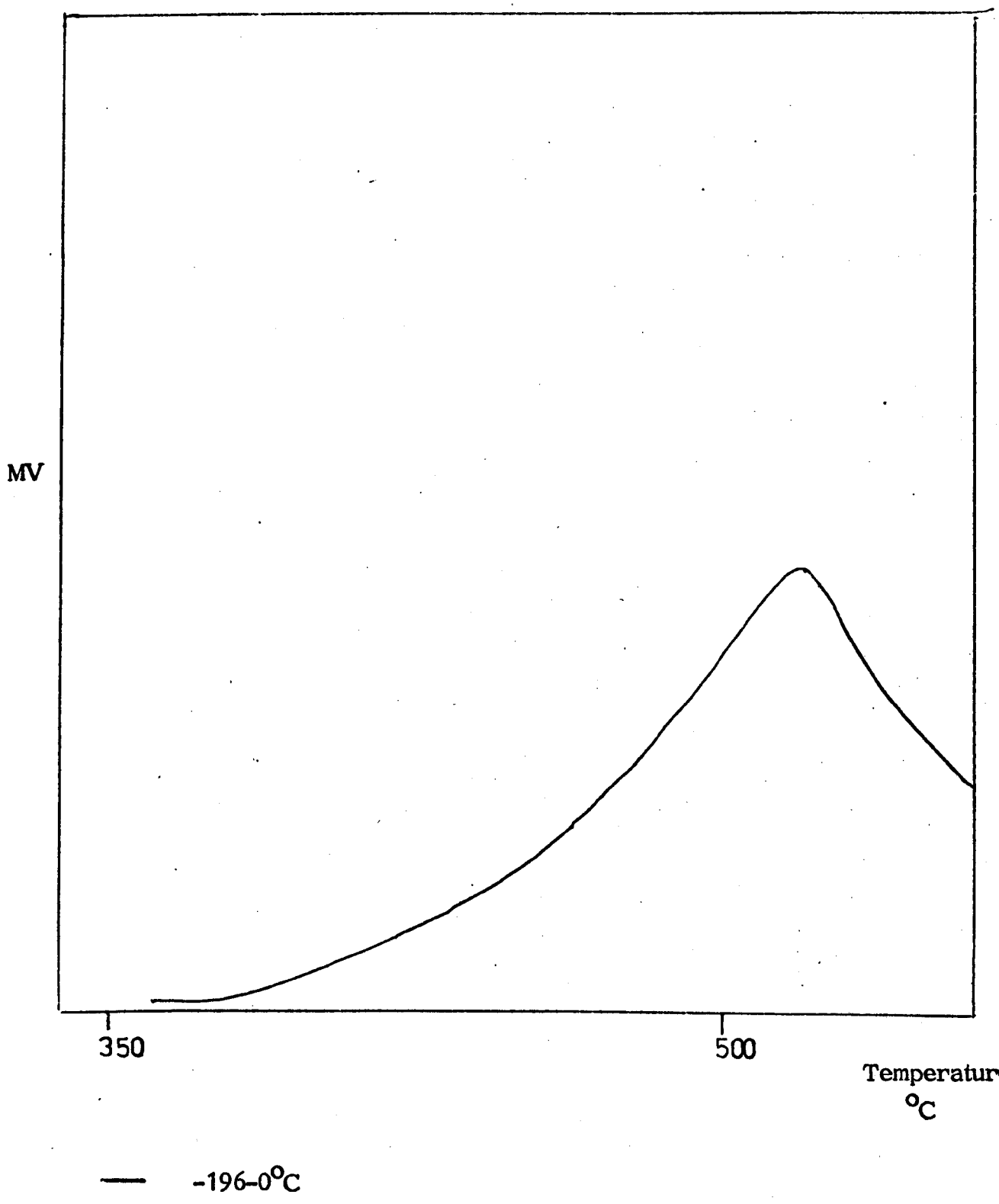
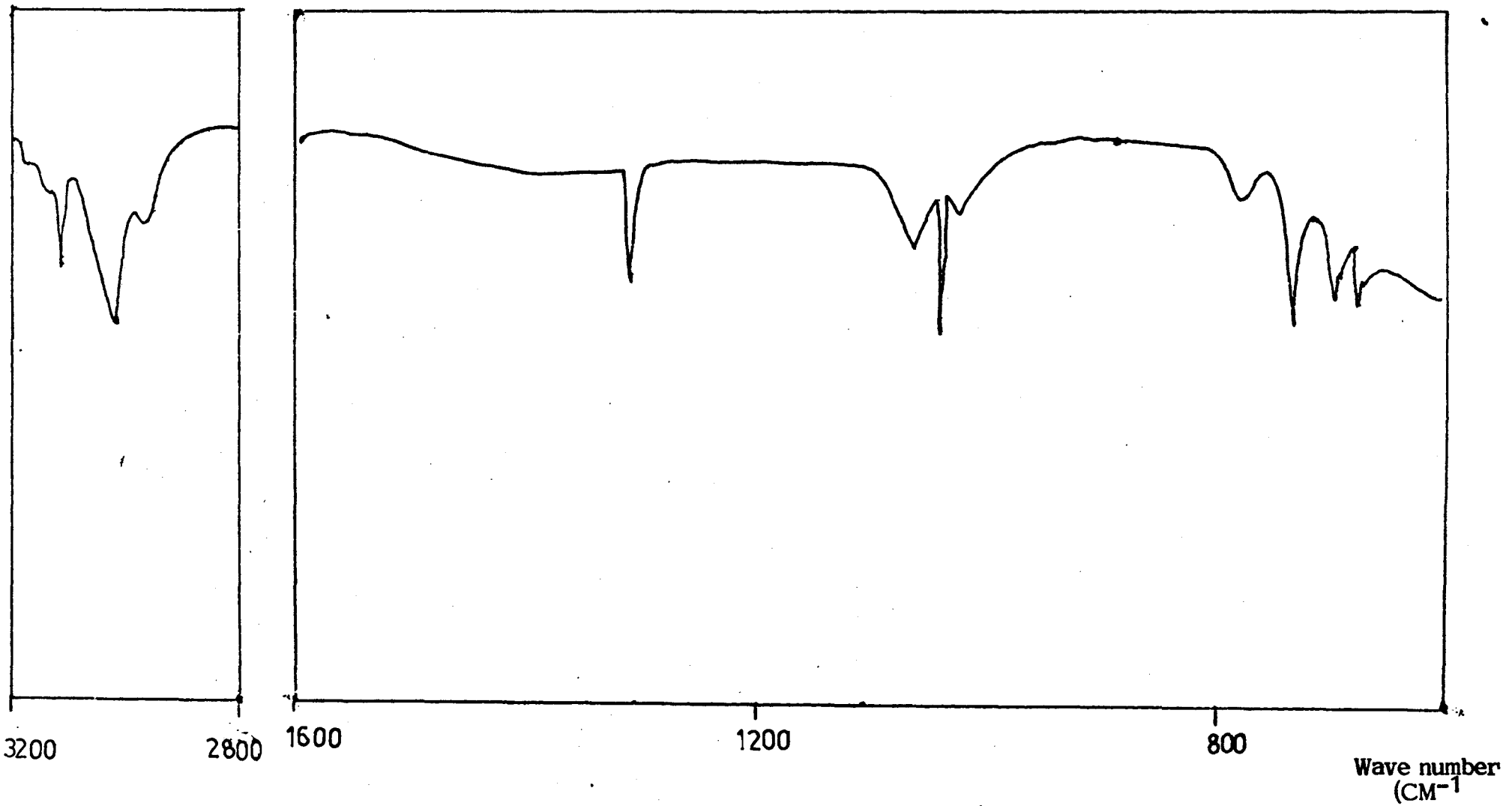


Figure 6.1

Figure 6.2



volatile products occurs at 509°C. Figure 6.2 illustrates the infrared spectrum of the volatile degradation products of this copolymer. Absorption at 3000 and 1310 cm^{-1} is strongly indicative of the presence of methane, while absorption at 1035 is attributed to the presence of methanol. Absorption at 660 cm^{-1} may be attributed to benzene while those at 695 and 730 cm^{-1} indicate the presence of a monosubstituted aromatic structure which is probably principally toluene.

The TVA thermogram of a copolymer obtained using a molar feed ratio of DMPX:Benzene 1:1 is illustrated on Figure 6.3. In this case the onset of volatilisation occurs at 310°C, products which are non-condensable at all trap temperatures being formed in large quantity. The rate of degradation is initially slow before a marked acceleration in rate occurs at 356°C reaching a maximum at 430°C. An overlapping peak with a maximum at 510°C indicates that degradation occurs in two well defined steps at two distinct temperatures. The TVA trace of the DMPX homopolymer is similar in many ways to that of the 1:1 copolymer, although the onset of volatilisation occurs at 185°C and the rate of volatilisation is significantly large at 300°C reaching maximum at 435°C. Again the trace reveals two overlapping peaks, the second of which has a maximum of 514°C. (Figure 6.4). Figure 6.5 illustrates the infrared spectrum of the volatile degradation products of the homopolymer. Absorption at 3005 cm^{-1} and 1310 cm^{-1} indicates the presence of methane and a characteristic absorption at 1035 cm^{-1} is due to methanol. The lack of absorption below 900 cm^{-1} indicates the absence of mono and disubstituted aromatic rings in the volatile products. This contrasts with products from the co-polymer which exhibit absorption at 660. 695 and 730 cm^{-1}.

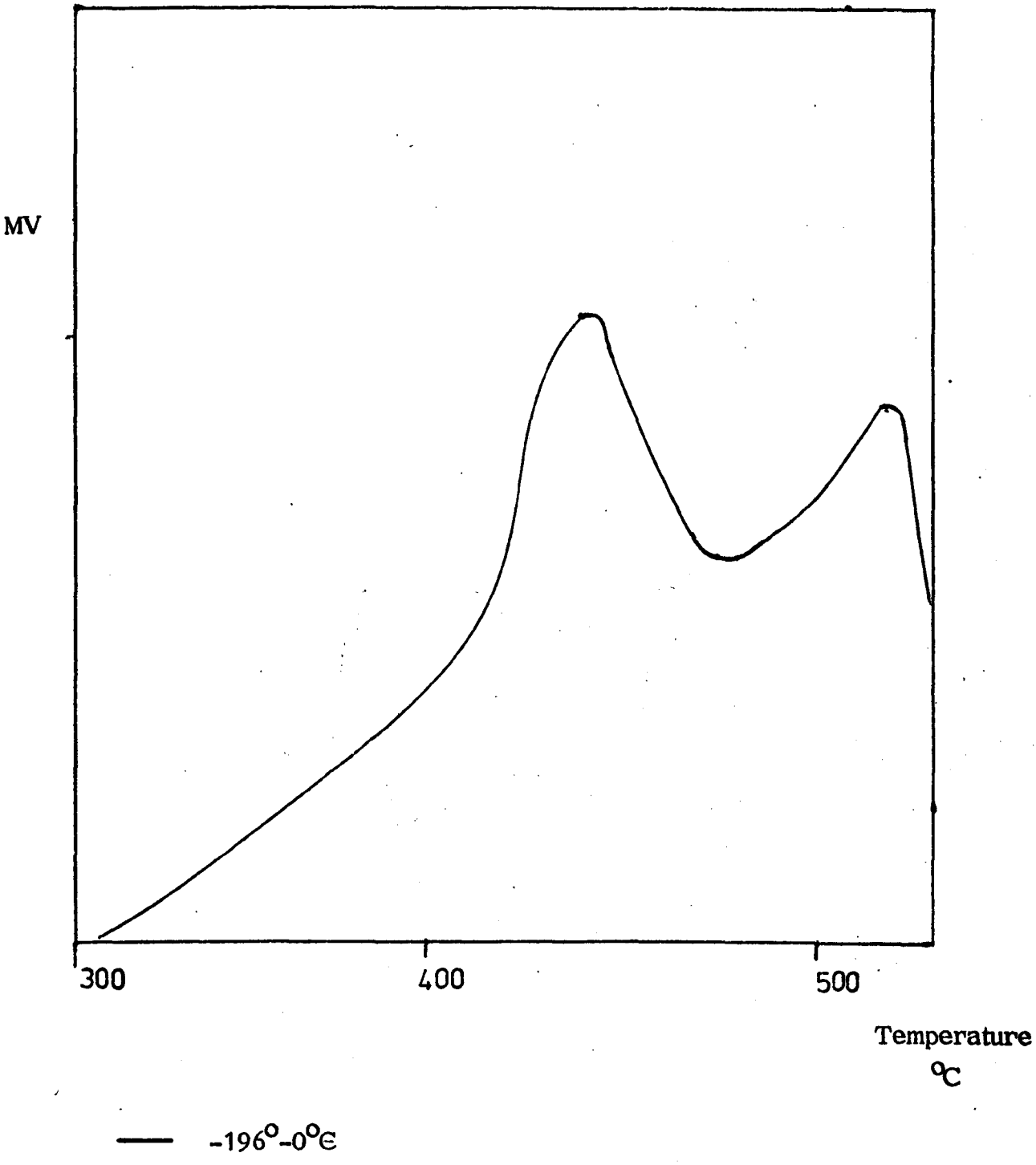


Figure 6.3

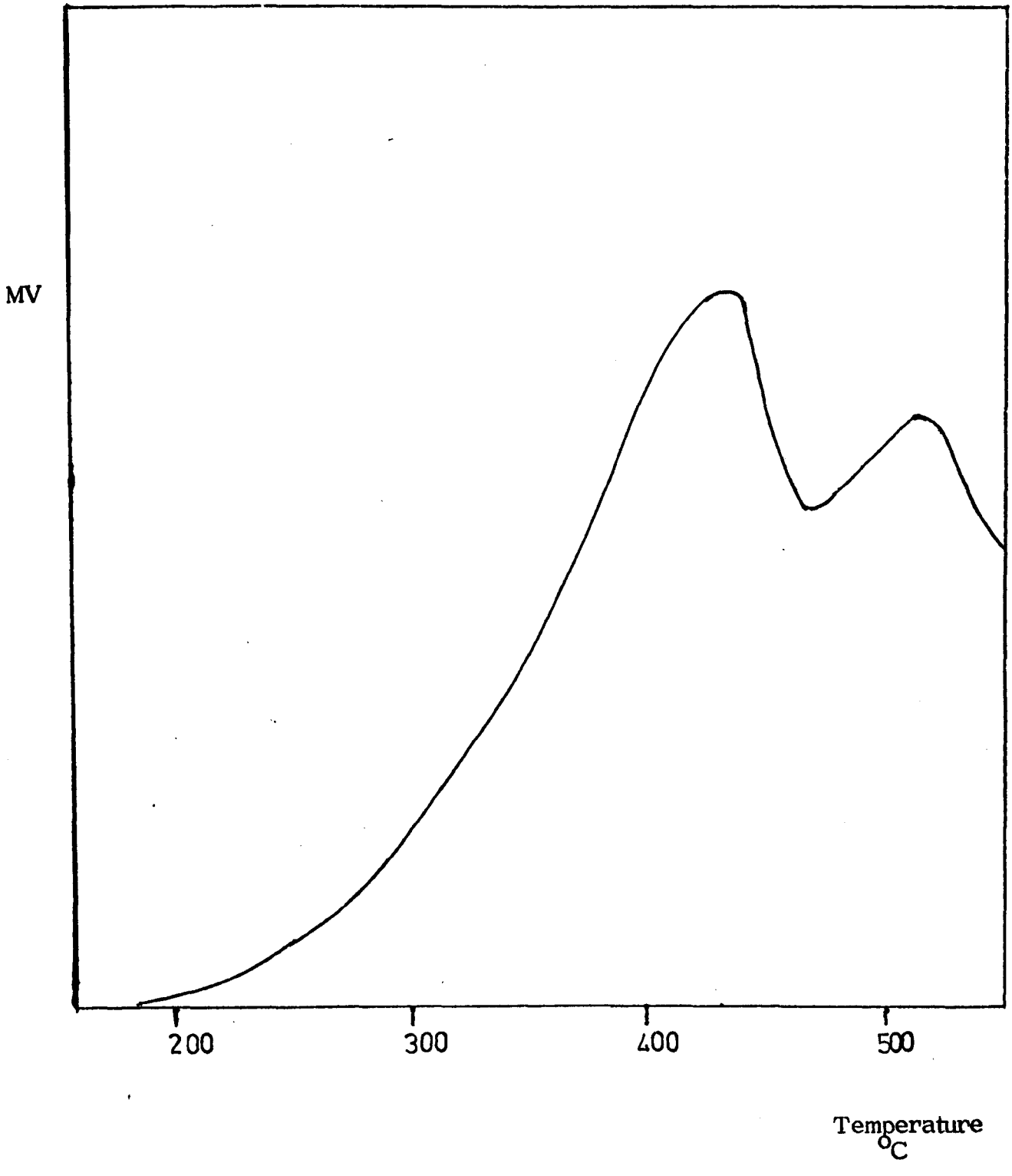


Figure 6.4

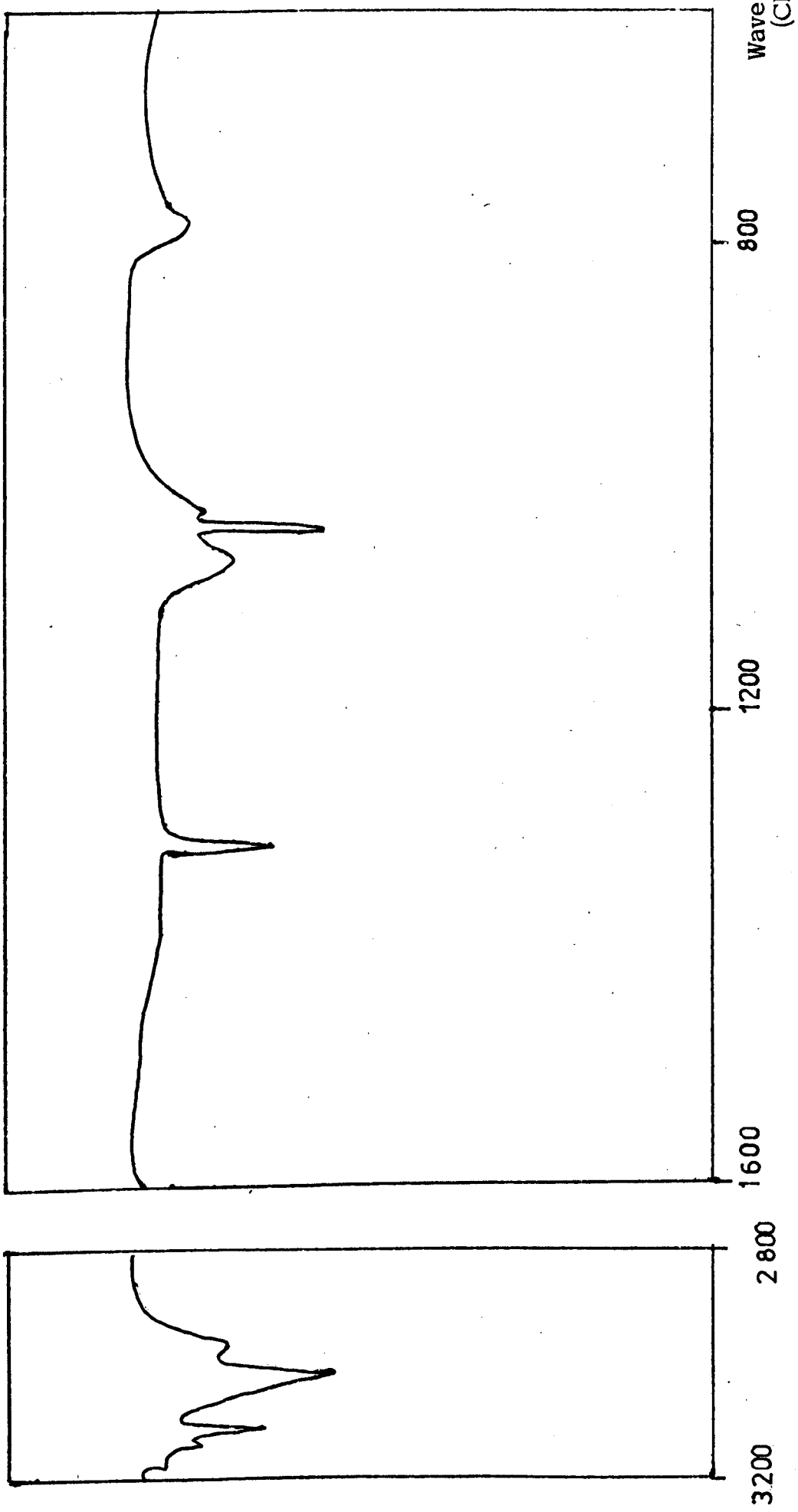


Figure 6.5

TVA degradation of the insoluble portion of co-polymer (5:1, Benzene:DMPX) increases slowly from 350°C to a maximum rate of evolution of volatile degradation products at a temperature in excess of 500°C (Figure 6.6). The TVA thermogram of the insoluble portion of homopolymer (Figure 6.7) reveals the onset of degradation at 313°C reaching a maximum at over 500°C. Infrared analysis of the products revealed that only methane is formed from the co-polymer but methane and methanol from the homopolymer.

6.5 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis was carried out on the homopolymer and of co-polymers of DMPX and benzene derived from a variety of molar feed ratios. All degradations were carried out under a dynamic nitrogen atmosphere at a programmed heating rate of 10°/min.

Figure 6.8 illustrates typical TGA curves of soluble co-polymers of DMPX and benzene and of the soluble portion of homopolymer while Figure 6. 9 compares the TGA curves of the insoluble portions of the 5:1 co-polymer and of the homopolymer.

Table 6.1 compares the thermal properties of the above polymers in terms of the temperature of onset of weight loss, temperature of maximum rate of degradation, percentage remaining at 500°C and at 800°C.

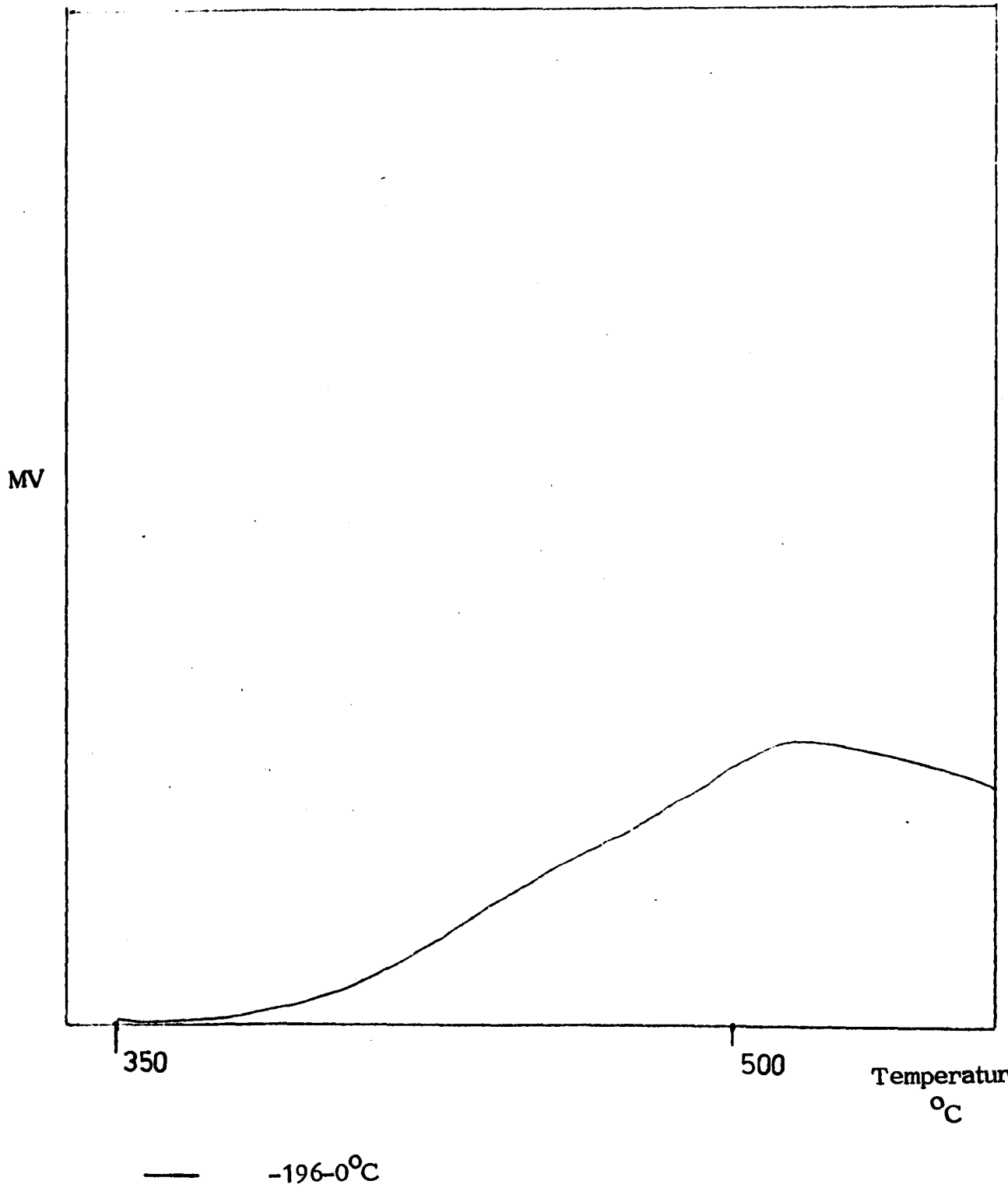


Figure 6.6

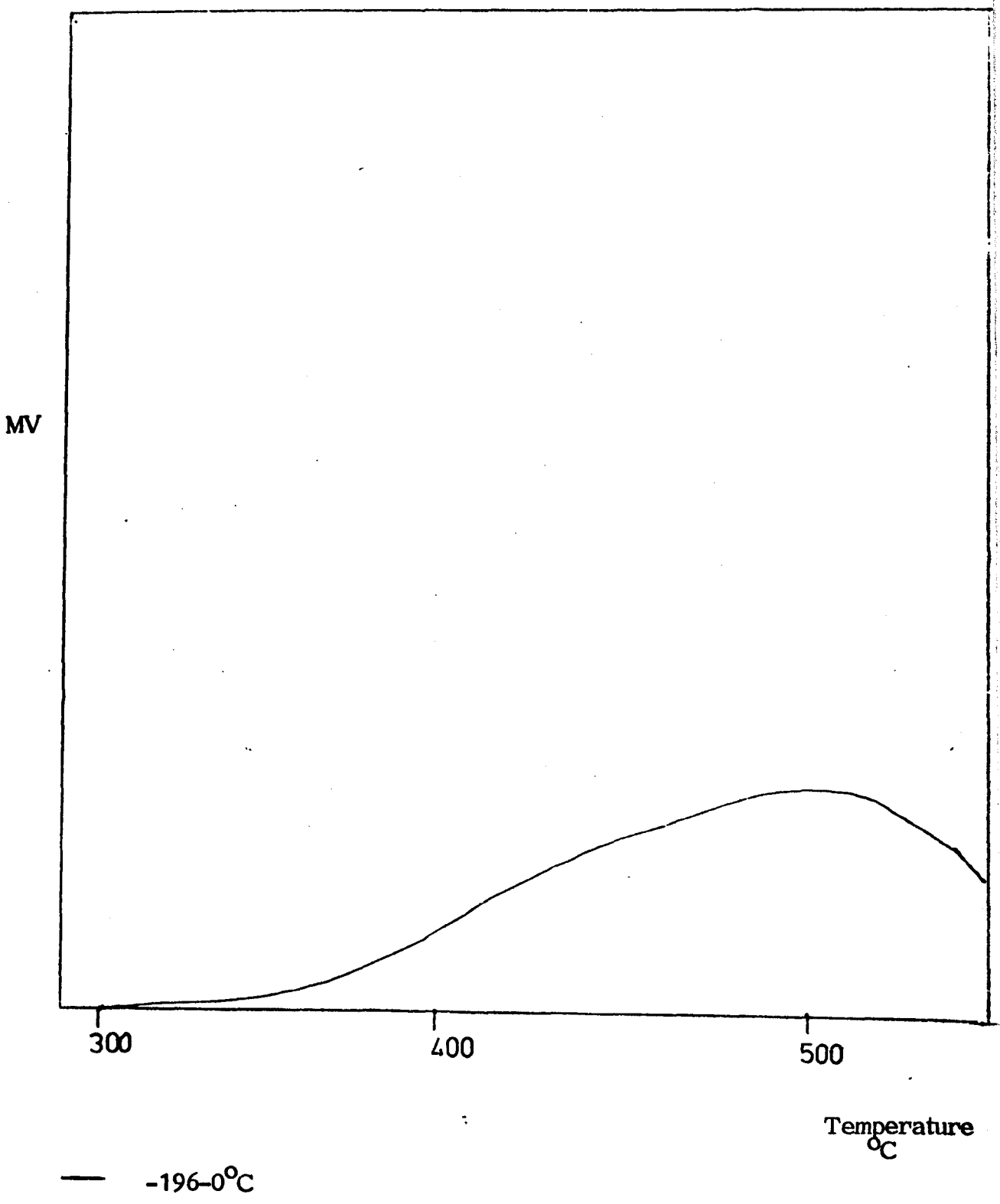


Figure 6.7

Figure 6.8

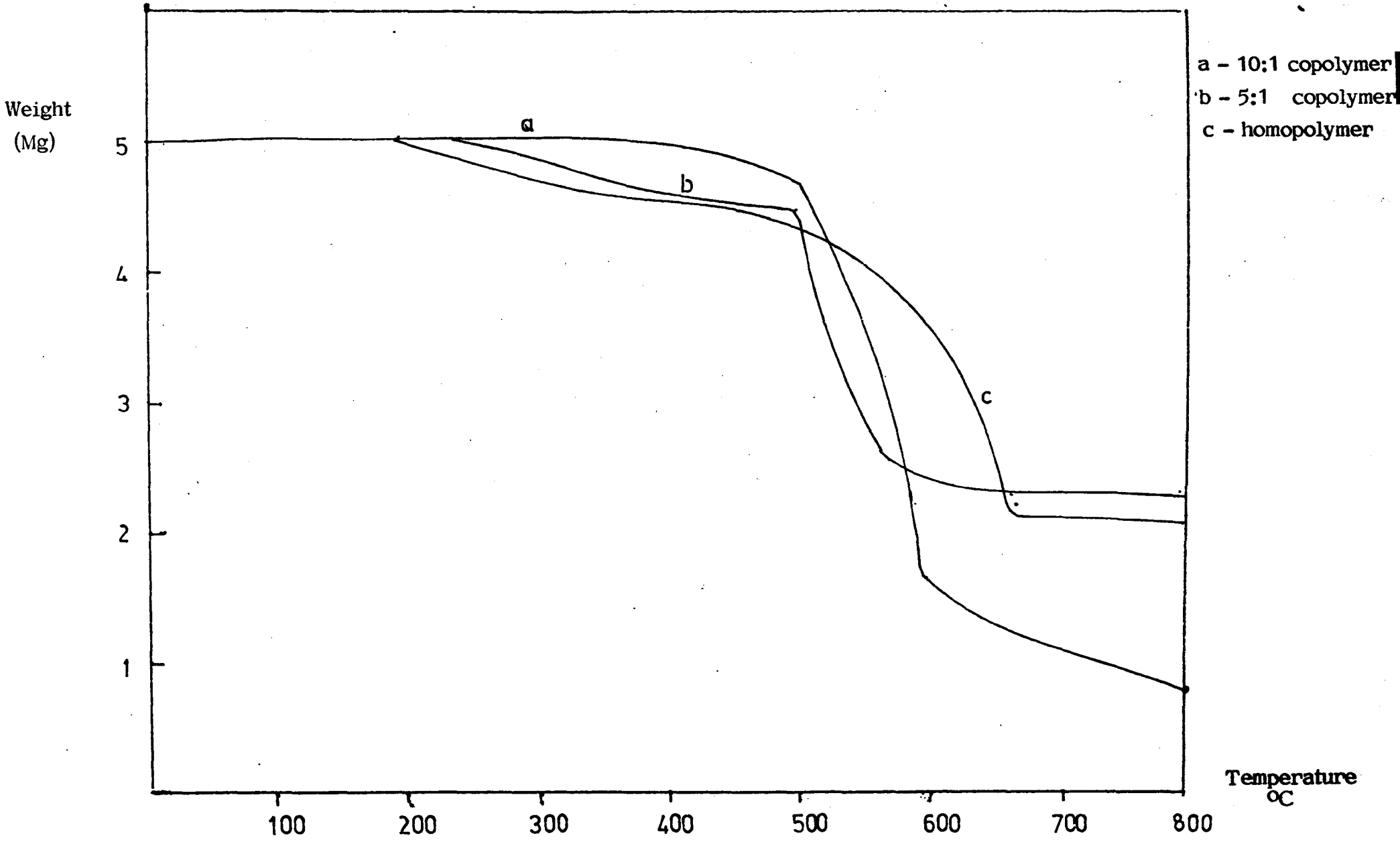

Weight
(Mg)
5
4
3
2
1
a
b
c
100
200
300
400
500
600
700
800
Temperature
°C
a – 10:1 copolymer
b – 5:1 copolymer
c – homopolymer

Figure 6.9

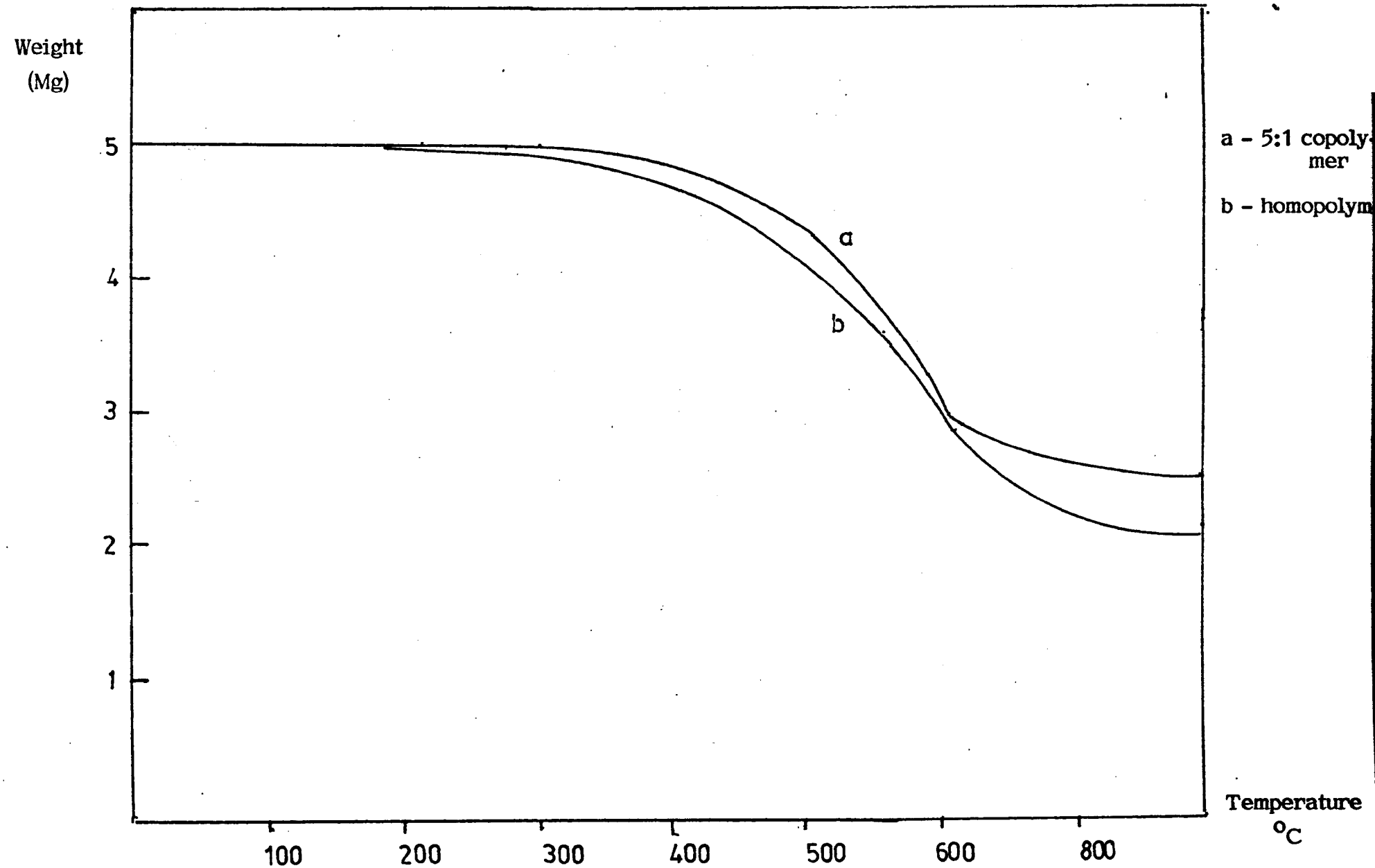

Weight
(Mg)
5
4
3
2
1
a
b
100
200
300
400
500
600
800
Temperature
°C
a - 5:1 copoly-
mer
b - homopolym

TABLE 6.1

Polymer	Onset of Degradation	Maximum rate of Degradation	% Weight loss at 500°C	% Weight loss at 800°C
Soluble 10:1 Co-polymer	400	550	7	86
Soluble 5:1 Co-polymers	230	520	12	52
Soluble Homopolymer	225	540	12	60
Insoluble 5:1 Co-polymer	300	550	7	49
Insoluble Homopolymer	120	550	12	54

6.6 Discussion

TVA and TGA analysis of polymer based on DMPX and benzene have shown that these polymers have high thermal stability in the range 200-300°C similar to those based on DCMB. It is therefore concluded that replacement of DMPX for DCMB in the monomer mixture does not have an adverse effect on the thermal properties of the resulting polybenzyl structures.

The stability of the insoluble portion of both co-polymers and homopolymers is undoubtedly due to a high degree of crosslinking. It is also apparent that crosslinking occurs in the course of degradation. The evolution of methanol indicates that pendant methoxyl groups participate in the crosslinking reaction, possibly by a cationic mechanism. The TVA of the homopolymer shows two peaks, the first of which is probably due largely to the evolution of methanol in the crosslinking reaction. However, volatile products, such as methane, which are non-condensable at -196°C are also evolved which indicates that degradation of the polymer chain is occurring in addition to crosslinking. The second peak in the TVA trace of the homopolymer is undoubtedly due to degradation of crosslinked material as this peak corresponds closely to the single peak obtained from TVA of the crosslinked homopolymer material.

Although there is only a single peak in the TVA thermogram degradation of the 5:1 co-polymer (Benzene: DMPX), it is likely that in this polymer a small amount of pendant methoxyl groups are present and that crosslinking occurs in the course of degradation. This suggestion is supported by the fact that methanol is detected by infrared in the degradation products of this polymer and in addition TGA reveals two distinct

zones of weight loss. The observation that 48% by weight of polymer in the TGA degradation of the 5:1 co-polymer remains at 800°C confirms the view that crosslinking occurs in the course of degradation. This is in contrast to the TGA degradation of the 10:1 co-polymer where only 14% by weight remains at 800°C. In this case the high ratio of benzene to DMPX in the initial reaction mixture results in the absence or in a very low concentration of methoxyl groups and hence crosslinking is not favoured in the course of this degradation.

It is therefore concluded that the optimum stability of polymers based on DMPX occurs when a small concentration of methoxyl groups are present, similar to the situation found in the 5:1 co-polymers. The reasons for the lower stability in the homopolymer are not clear and further investigation is necessary to account for this observation.

CHAPTER 7

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1 General Discussion

It was mentioned in Chapter one that the overall objective of this work was to examine the kinetics of the initial stages of the co-polymerisation of DMPX and benzene and to relate this to the properties of the final polymer.

It was envisaged that the simple kinetic treatment, applied to the co-polymerisation of DCMB and benzene, could be used for the DMPX system, so that a direct comparison of results for the two systems could be made. Unfortunately, owing to difficulties associated with the co-polymerisation of DMPX and benzene described in Chapter three, direct comparison of the kinetics of the two systems was not possible. It was, however, possible to estimate the relative reactivities of the monomer DMPX and the dimeric product (11) by measuring the rate constants of the first two stages of polycondensation. For the co-polymerisation of DMPX and benzene the ratio k_2/k_1 is of the order of two, whereas with DCMB this ratio is over ten.

This high reactivity of the chloromethyl groups on the dimeric products of DCMB and benzene relative to the two in DCMB is reflected in the structure of the final polymer. If we assume that pendant chloromethyl groups in all products are highly reactive, then it is reasonable to propose that long chain branches and crosslinking between the chains is favoured.

This is the picture proposed by Grassie and Meldrum[16-23]. In the present work it has been shown that the reactivity of the dimeric products of DMPX and benzene condensation is greater than that of the monomer but to a much lesser extent. As a consequence, it would be expected that chain branches would be shorter and that crosslinking would be low. Spectroscopic evidence has shown that branching occurs to a high degree in polymers derived from benzene and DMPX but also points to these branches being shorter in length. This is again consistent with the kinetic data discussed above.

It was initially envisaged, that the differences in structure of DCMB and DMPX based polymers would lead to a significant variation in their thermal properties. It has been found, however, that polymers based on DMPX have similar stability to those based on DCMB. For example, it has been shown[15] by TVA, that degradation of a co-polymer of DCMB and benzene commences at 330°C while in the present work, it has been shown that a corresponding co-polymer of DMPX and benzene, is stable to 360°C. TVA and TGA have also shown that the insoluble portions of DMPX based polymers are considerably more stable than those of DCMB.

It is therefore clear from this work, that polymers based on DMPX are superior for commercial exploitation. Obvious problems are associated with the evolution of hydrogen chloride in an industrial process and although a process has been adapted for DCMB polymerisation[14], it has been found to be highly endothermic. Although it has been found using DTA that DMPX based polymers do not have a definite melting point and moulding or extrusion is not possible, the solubility of these polymers is an added advantage in industrial processing. Clearly the evolution of methanol is preferred to evolution of hydrogen chloride.

7.2 Suggestions for Future Work

In the present work, the mechanism of the co-polymerisation of DMPX and benzene has been investigated in conjunction with analysis of the structure of the final polymer. Only limited thermal analysis of DMPX based polymers has been carried out and it is in this direction that future work should be directed.

It has been shown previously[24,25] that co-polymerisation of DCMB with heterocyclic aromatic compounds, in particular thiophene, can enhance thermal stability. For this reason, it would be worthwhile to compare the thermal stability of the co-polymer of DMPX and benzene with the stability of co-polymers of DMPX and heterocyclic co-monomers. It has been proposed that the high reactivity of the thiophene nucleus promotes intramolecular cyclicisation to produce a partial ladder structure and enhanced stability. It would therefore be interesting to see if this effect is reproduced in the co-polymerisation of DMPX and thiophene. In addition to co-polymerisation with heterocyclic compounds, it would be worthwhile to investigate co-polymers of DMPX and aromatic co-monomers which areactivated towards substitution by electron donating substituents. An example of this is the co-polymer of DMPX and phenol which is produced commercially. Thermal studies of this co-polymer and of others containing activated aromatic nuclei such as aniline or toluene would be of interest.

From an academic point of point, it would be of interest to compare, by kinetic methods, the relative reactivities of various co-monomers towards DMPX. The results of such an investigation could then be related to the stability of the final polymer. However, the difficulties associated with the kinetic examination of DMPX polymerisations would make it extremely time consuming.

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